Remedial Investigation/Feasibility Study Work Plan

Pines Area of Investigation
AOC II
Docket No. V-W-'04-C-784

Volume 3
Quality Assurance Project Plan

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QUALITY ASSURANCE PROJECT PLAN
REMEDIAL INVESTIGATION AND FEASIBILITY STUDY
PINES AREA OF INVESTIGATION
Revision 4
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AOC I	Administrative Order on Consent, 2003 and as amended, 2004; Docket No. V-W-03-730
AOC II	Administrative Order on Consent, 2004; Docket No. V-W-’04-C-784
AWQC	Ambient Water Quality Criteria
bgs	Below Ground Surface
CAS	Columbia Analytical Services
CCB	Coal Combustion By-product
CCBK	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CLP	Contract Laboratory Program
COC	Chain of Custody
CSM	Conceptual Site Model
CVAAS	Cold Vapor Atomic Absorption Spectrometry
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOE	Department of Energy
DOT	Department of Transportation
DQL	Data Quality Level
DQO	Data Quality Objective
EDD	Electronic Data Deliverable
ENSR	ENSR Corporation
EPC	Exposure Point Concentration
ERA	Ecological Risk Assessment
ESL	Ecological Screening Level
ESSL	Ecological Soil Screening Level
FS	Feasibility Study
FSP	Field Sampling Plan - Volume 2 of the RI/FS Work Plan
GEL	General Engineering Laboratory
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
GPS	Global Positioning System
GTC	Geochemical Technologies Corporation
HA	Health Advisory
HASP	Health and Safety Plan
HHRA	Human Health Risk Assessment
IATA	International Air Transport Association
ICAO	International Civil Aviation Organization

ICBK	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICV	Initial Calibration Verification
ID	Identification
IDEM	Indiana Department of Environmental Management
IDNL	Indiana Dunes National Lakeshore
IDNR	Indiana Department of Natural Resources
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
MARLAP	Multi-Agency Radiological Laboratory Analytical Protocols Manual
MBAs	Methylene Blue Substances
MCL	Maximum Contaminant Level
MDA	Minimum Detectable Activity
MDL	Method Detection Limit
mg/kg	Milligram per Kilogram
mg/L	Milligram per Liter
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MSR	Management System Review
MWSE	Municipal Water Service Extension
NCP	National Contingency Plan
NIPSCO	Northern Indiana Public Service Company
ORP	Oxidation-Reduction Potential
ORNL	Oak Ridge National Laboratory
OSWER	Office of Solid Waste and Emergency Response
pCi/L	Picocuries per Liter
PE	Performance Evaluation
PRG	Preliminary Remediation Goal
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
QMP	Quality Management Plan
%R	Percent Recovery
RAL	Removal Action Level
RAO	Remedial Action Objective
RI	Remedial Investigation
RI/FS	Remedial Investigation and Feasibility Study
RL	Reporting Limit

RPD	Relative Percent Difference
RPM	Remedial Project Manager
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan
SMS	Site Management Strategy
SOP	Standard Operating Procedure
SOW	Statement of Work
TIMS	Thermal Ionization Mass Spectrometry
TBD	To Be Determined
TSA	Technical System Audit
TSS	Total Suspended Solids
TOC	Total Organic Carbon
TU	Tritium Units (3.2 pCi/L)
ug/kg	Micrograms per Kilogram
UMTL	University of Miami Tritium Laboratory
US	United States
uS	Micro Siemens
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USFWS	United States Fish and Wildlife Service
WQS	Indiana State Water Quality Standards

STANDARD CHEMICAL ABBREVIATIONS

Al	Aluminum
Ag	Silver
As	Arsenic
B	Boron
Ba	Barium
Be	Beryllium
Ca	Calcium
Cd	Cadmium
Cl	Chloride
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
F	Fluoride
Fe	Iron
K	Potassium
Hg	Mercury
Li	Lithium
Mg	Magnesium
Mo	Molybdenum
Mn	Manganese
Na	Sodium
NH_3	Ammonia
Ni	Nickel
Pb	Lead
Ra	Radium
S	Sulphur
Sb	Antimony
Se	Selenium
Si	Silicon
Sr	Strontium
U	Uranium
V	Vanadium
Zn	Zinc
$CaCO_3$	Calcium Carbonate

Cl	Chloride
F	Fluoride
HCO_3	Bicarbonate
$HN0_3$	Nitric Acid
NH_4	Ammonium
NO_3	Nitrate
PO_4	Phosphate
SO_2	Sulfur dioxide
SO_4	Sulfate

DISCLAIMER

This document is a document prepared under a federal administrative order on consent and revised based on comments received from the U.S. Environmental Protection Agency (USEPA). This document has been approved by USEPA, and is the final version of the document.

SECTION A – PROJECT MANAGEMENT

A1 Introduction

In April 2004, the United States Environmental Protection Agency (USEPA) and the Respondents (Brown Inc., Ddalt Corp., Bulk Transport Corp., and Northern Indiana Public Service Company (NIPSCO)) signed an Administrative Order on Consent (AOC II) (Docket No. V-W-'04-C-784) to conduct a Remedial Investigation and Feasibility Study (RI/FS) at the Pines Area of Investigation, or Area of Investigation as set forth in Exhibit I to AOC II located in the environs of the Town of Pines, Indiana. AOC II (Section VII. 20) and the Statement of Work (SOW) (Task 2.1), which is provided as an attachment to AOC II, require the Respondents to develop an RI/FS Work Plan. The RI/FS Work Plan has been developed in seven volumes, as follows:

- Volume 1 - Work Plan Overview.
- Volume 2 – Field Sampling Plan (FSP).
- Volume 3 - Quality Assurance Project Plan (QAPP).
- Volume 4 - Health and Safety Plan (HASP).
- Volume 5 - Human Health Risk Assessment (HHRA) Work Plan.
- Volume 6 - Ecological Risk Assessment (ERA) Work Plan.
- Volume 7 - Quality Management Plan (QMP).

This document provides the QAPP for the Pines Area of Investigation, and serves as Volume 3 of the RI/FS Work Plan. The QAPP has been prepared to follow the requirements in AOC II and the SOW, as well as to be compliant with the National Contingency Plan (NCP) (USEPA, 1990). The QAPP incorporates the FSP (Volume 2 of the RI/FS Work Plan) by reference.

This QAPP presents the organization, objectives, planned activities, and specific quality assurance/quality control (QA/QC) procedures associated with the RI/FS. Specific protocols for sampling, sample handling and storage, chain-of-custody, and laboratory and field analyses are described. All QA/QC procedures are structured in accordance with applicable technical standards, USEPA's requirements, regulations, and guidance. This QAPP has been prepared in accordance with the USEPA QAPP policy as presented in the Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan (USEPA, 2000a).

A2 Project Schedule

The project schedule is presented in Volume 1 Section 5.0 of the RI/FS Work Plan.

A3 Distribution List

The QAPP, and any subsequent revisions, will be distributed to the personnel shown on the Distribution List that immediately follows the approval page.

A4 Project/Task Organization

The lines of authority and communication specific to the Quality Assurance (QA) program for this Remedial Investigation (RI) are presented in Figure A-1. The responsibilities of key personnel are described below.

A4.1 Management Responsibilities

USEPA Region 5 Remedial Project Manager (RPM)

The USEPA Region 5 RPM, Timothy Drexler, has the overall responsibility for all phases of the investigation.

Respondents' Project Managers

The Project Managers for the individual Respondents are Dan Sullivan of NiSource and Val Blumenfeld of Brown Inc. They will be responsible for project direction and decisions concerning technical issues and strategies, budget, and schedule.

ENSR Project Manager

ENSR Corporation (ENSR) is retained by the Respondents and has been approved by USEPA as the environmental consultant conducting the remedial investigations, risk analysis and the feasibility study for the Pines Area of Investigation. The ENSR Project Manager, Lisa JN Bradley, will be responsible for technical, financial, scheduling matters and for timely delivery of all products/results pertaining to the RI/FS. The ENSR Project Manager also will be responsible for project coordination between the Respondents and USEPA as required.

ENSR RI Task Manager

The ENSR RI Task Manager, Elizabeth Perry, will have the overall responsibility for implementing the sampling activities described in this RI/FS Work Plan and for reporting these activities in the RI Report. Specific responsibilities of the ENSR RI Task Manager will include, but not be limited to, the following:

- Providing personnel and equipment for investigation activities;
- Ensuring that ENSR's associates perform their designated duties in accordance with the FSP and the HASP (Volume 4 of this RI/FS Work Plan);
- Ensuring required QA/QC procedures are properly implemented and documented;
- Ensuring that sampling activities are properly carried out and completed within the approved schedule;
- Communicating any request for modifications, if necessary, to the approved FSP to the ENSR Project Manager; and
- Promptly notifying the ENSR Project Manager if unforeseen field conditions and/or analytical issues are encountered that affect achievement of the project data quality objectives (DQOs).

Ms. Perry is also a Professional Geologist licensed to practice in Indiana. All geologic-related work (e.g., logging, well installation) will be performed under her direction. While she may not be in the field directly conducting the work, she must review and approve all such work.

ENSR Health and Safety Manager

The ENSR Regional Health and Safety Manager, Joseph Sanders, will be responsible for ensuring the objectives of ENSR's corporate health and safety program are carried out. The ENSR Regional Health and Safety Manager will also be responsible for the coordination and communication of health and safety issues for field personnel.

A4.2 Quality Assurance Responsibilities

ENSR Project QA Officer

The ENSR Project QA Officer, Debra (McGrath) Simmons, has the overall responsibility for quality assurance. The ENSR Project QA Officer communicates directly to the ENSR Project Manager on matters pertaining to QA, data validation, and laboratory analyses. Specific responsibilities include:

- Reviewing and approving the QAPP;
- Reviewing and approving QA procedures, including any modifications to existing approved procedures;
- Ensuring that QA audits of the various phases of the project are conducted as required by this QAPP;
- Providing technical assistance to project staff;
- Ensuring that data validation/data assessment is conducted in accordance with the QAPP; and
- Reporting on the adequacy and efficiency of the QA Program to the ENSR Project Manager and recommending corrective actions, if necessary.

ENSR Data Validator

The ENSR Data Validator reports to the ENSR Project QA Officer. The Data Validator is responsible for validating the analytical data in accordance with the QAPP.

USEPA Region 5 Quality Assurance Plan Reviewer

The USEPA Region 5 Quality Assurance Plan Reviewer, Warren Layne, has the responsibility to review and approve all QAPPs. Additional USEPA responsibilities include:

- Conducting external performance and system audits of the selected laboratory;
- Evaluating results of performance evaluation sample data; and
- Reviewing and evaluating analytical field and laboratory procedures.

A4.3 Laboratory Responsibilities

Columbia Analytical Services (CAS), located in Rochester, NY, will perform the analyses of all groundwater, surface water, suspected CCB materials, sediment, and private well water samples with the exception of the following:

- The radionuclide analyses, sediment grain size distribution, sediment bulk density tests, and analysis of boron and uranium by inductively coupled plasma-mass spectrometry (ICP-MS) will be performed by General Engineering Laboratories LLC (GEL), located in Charleston, SC.
- The University of Miami Tritium Laboratory (UMTL), located in Miami, FL will perform the low-level tritium analyses.
- The boron isotope analyses will be performed by Geochemical Technologies Corporation (GTC), located in Golden, CO.
- Test America (formerly STL) Valparaiso located in Valparaiso, IN, will perform the bacteriological parameters, specifically total coliform and Escherichia Coli.

Laboratory Director

The Laboratory Directors are ultimately responsible for the data produced by their laboratories. Specific responsibilities include:

- Resources are adequately allocated to specific projects and that sufficient staffing, equipment, and support are provided.
- Overseeing the technical operations' Section Managers and the Laboratory QA Manager.

The Laboratory Directors are Mike Perry (CAS), Carey Bocklet (GEL), R.L. Bassett, Ph.D. (GTC), James Happell, Ph.D. (UMTL), and Kurt Ill (Test America Valparaiso).

Section Manager

The individual Laboratory Section Managers report to the Laboratory Director. Specific responsibilities include:

- Supervision of employees within their specific analytical area;
- Overseeing and supporting the development, implementation, and operation of analytical technical programs;
- Coordinating sample flow and for implementing QA and QC activities in their area of authority; and
- Working in conjunction with the Laboratory QA Manager to ensure that QA/QC recommendations are reviewed and that corrective actions are implemented and effective.

Laboratory QA Manager

The Laboratory QA Manager reports to the Laboratory Director. Specific responsibilities include:

- Monitoring the QA and QC activities of the laboratory to ensure conformance with authorized policies, procedures, and good laboratory practices, and recommending improvements as appropriate;
- Informing specific Section Managers of noncompliance with the approved QA/QC criteria;
- Ensuring that all records, logs, Standard Operating Procedures (SOPs), project plans, and analytical results are maintained in a retrievable fashion; and
- Ensuring that SOPs and other controlled documents are distributed to all appropriate laboratory personnel for use in the project.

The Laboratory QA Managers are Lisa Reyes (CAS), Robert Pullano (GEL), R.L. Bassett, Ph.D. (GTC), Charlene Grall (UMTL), and Linda Moore (Test America Valparaiso).

Laboratory Project Manager

The Laboratory Project Manager is ultimately responsible for all laboratory analyses and is the primary point of contact for issues surrounding this QAPP, including resolving technical problems, modifications to SOPs, etc. The Laboratory Project Manager is responsible for the coordination of routine day-to-day project activities including project initiation, status tracking, data review and requests, inquiries and general communication related to the project. Final approval of data packages is the responsibility of the Laboratory Project Manager.

The Laboratory Project Manager is the primary point of contact between the laboratory and ENSR. Specific responsibilities of the Laboratory Project Manager include:

- Monitoring analytical and QA project requirements for a specified project;
- Acting as a liaison between ENSR and the laboratory staff;
- Reviewing project data packages for completeness and compliance to ENSR needs;
- Monitoring, reviewing, and evaluating the progress and performance of projects; and
- Providing all analytical deliverables to ENSR in a timely manner.

The Laboratory Project Managers are Janice Jaeger (CAS), Edith Kent (GEL), R.L. Bassett, Ph.D. (GTC), Charlene Grall (UMTL), and Adrienne Byrnes (Test America Valpariaso).

Laboratory Staff

Laboratory staff includes the Laboratory Director, the Laboratory Supervisor, Section Managers, Group Leaders, Chemists, and Technicians. These individuals are responsible for the actual preparation, analysis, reporting, and reviewing of the analytical information. The analysts are responsible for understanding and implementing SOPs and for conformance with the Quality Assurance Program. Analysts are also responsible for the initial review of data that they generate during the analytical process and the identification of nonconforming events within their scope of concern. These individuals, in conjunction with laboratory management and the laboratory QA Manager, may also be responsible for implementing corrective actions.

Sample Receipt Personnel

Sample receipt personnel, or sample custodians, are responsible for the initial assessment of samples, including documentation of sample conditions upon receipt, and accuracy and clarity of requests on the Chain-of-Custody (COC) forms that accompany the samples. Sample receipt personnel, along with laboratory management, are responsible for the resolution and documentation of any issues associated with the initial assessment of the sample integrity on arrival. Resolution may include discussions with laboratory personnel, client contacts, and/or laboratory management.

Following the initial assessment, sample receipt personnel are responsible for the accurate input of sample information into the data management system and the assignation of laboratory batch identification and individual sample identifiers. Sample receipt personnel also initiate the internal COC process and begin laboratory tracking.

Sample custodians are Greg Esmerian (CAS), Pete Wilber (GEL), R.L. Bassett, Ph.D. (GTC), Charlene Grall (UMTL), and Chris Chavis (Test America Valparaiso).

A4.4 Field Responsibilities

ENSR Field Operations Leader

The ENSR Field Operations Leader, Lisa Graczyk, has overall responsibility for completion of all field activities in accordance with the FSP and QAPP and is the communication link between the ENSR RI

Task Manager and the field team. Specific responsibilities of the ENSR Field Operations Leader include:

- Coordinating activities in the field;
- Assigning specific duties to field team members;
- Mobilizing and demobilizing of the field team and subcontractors to and from the Area of Investigation;
- Directing the activities of subcontractors at the Area of Investigation;
- Resolving any logistical problems that could potentially hinder field activities, such as equipment malfunctions or availability, personnel conflicts, or weather dependent working conditions; and
- Implementing field QC including issuance and tracking of measurement and test equipment; the proper labeling, handling, storage, shipping, and COC procedures used at the time of sampling; and control and collection of all field documentation.

ENSR Field Staff

The field staff reports directly to the ENSR Field Operations Leader. The responsibilities of the field staff include:

- Collecting samples, conducting field measurements, and decontaminating equipment according to documented procedures stated in the FSP;
- Ensuring that field instruments are properly operated, calibrated, and maintained, and that adequate documentation is kept for all instruments;
- Collecting the required QC samples and thoroughly documenting QC sample collection;
- Ensuring that field documentation and data are complete and accurate; and
- Communicating and documenting any nonconformance or potential data quality issues to the ENSR Field Operations Leader as well as documenting subsequent corrective action and effectiveness of corrective action.

Subcontractors

ENSR subcontractors will perform drilling and surveying, activities among others. The subcontractors are responsible for conducting the work in accordance with the project plans and contractual agreements and for communicating any issues concerning the budget, schedule, or achievement of the technical specifications to the ENSR Field Operations Leader.

A5 Problem Definition and Background

A5.1 Site Background and Description

Between 2000 and 2004, the Indiana Department of Environmental Management (IDEM) and USEPA responded to homeowners by conducting sampling of private water supply wells in a portion of the Town of Pines. In some of these samples, boron (B) and molybdenum (Mo) were detected at concentrations above USEPA's Removal Action Levels (RALs) (USEPA, 1998). These concentrations in groundwater are suspected by the USEPA to be derived from coal combustion by-products (CCBs). CCBs have been disposed at a permitted Restricted Waste Facility known as Yard 520, and CCBs are suspected to have been used as fill in areas within the Area of Investigation outside of Yard 520. Yard 520 is operated by Brown Inc., and most of the CCBs at Yard 520 were generated during combustion of coal at NIPSCO's Michigan City Generating Station.

To address the boron and molybdenum detections above the USEPA RALs, the Respondents agreed to extend the municipal water service from Michigan City to selected portions of the Town of Pines. This agreement was documented in an Administrative Order on Consent, referred to as AOC I. Additional sampling of other private wells indicated some concentrations near or exceeding USEPA RALs. To address this, the Respondents voluntarily approached the USEPA to discuss extending the municipal water service to a larger area under an amendment to AOC I.

The Respondents also signed AOC II to conduct an RI/FS for the Area of Investigation, as identified in the Order. Under the SOW, Task 1 is the preparation of a Site Management Strategy (SMS). A draft SMS document, which outlined a preliminary conceptual model, data gaps, and the strategy for certain elements of the RI/FS, was submitted in June 2004. The SMS was conditionally approved by USEPA in November 2004. Task 1 of the SOW was completed with the submission of the Final SMS in January 2005 (ENSR, 2005a). The SMS serves as the basis for development of the RI/FS work plans prepared under Task 2 of the SOW, including this QAPP.

A5.2 Problem Definition

The overall objectives of the RI/FS for the Pines Area of Investigation are as follows:

(a) To determine the nature and extent of constituents in the Area of Investigation and any threat to the public health, welfare, or the environment caused by releases or threatened releases of constituents related to CCBs at or from the Area of Investigation by conducting a RI.

(b) To collect data necessary to adequately characterize, for the purpose of developing and evaluating effective remedial alternatives, the following:

   i) Whether the water service extension installed pursuant to AOC I and AOC I as amended is sufficiently protective of current and reasonable future drinking water use of groundwater in accordance with Federal, State, and local requirements;

   ii) Whether there are significant human health risks at the Area of Investigation associated with exposure to CCBs; and

   iii) Whether CCB-derived constituents may be causing unacceptable risks to ecological receptors.

(c) To determine and evaluate alternatives for remedial action to prevent, mitigate, control or eliminate risks posed by any release or threatened release of constituents related to CCBs at or from the Area of Investigation, by conducting an FS.

Implementation of the RI will provide the data necessary to conduct the HHRA and ERA to appropriately evaluate potential current and reasonably foreseeable future risks to human health and ecological receptors. If an unacceptable risk is identified, the FS will evaluate the alternative remedial actions to address the risk.

A6 Project/Task Description

As noted above, the purpose of the RI is to obtain the data necessary to appropriately evaluate potential current and reasonably foreseeable future risks to human health and ecological receptors. The QA/QC procedures specified in this QAPP are intended to meet these objectives, including addressing the general data gaps and strategy items identified in the SMS (ENSR, 2005a). As discussed in detail in the FSP, the RI will include the following components:

- Characterization of potential sources, including distribution of CCBs;
- Geologic/hydrogeologic characterization, including conducting fate and transport analyses of CCB-derived constituents;
- Characterization of groundwater/surface interactions;
- Characterizing the nature and extent of CCB-derived constituents in groundwater and other media; and
- Characterization of ecosystems/habitats.

The work to be performed for each of these evaluations is discussed in detail in Section 2 of the FSP and summarized below.

A6.1 Evaluation of CCBs as Potential Sources

CCBs have been identified as potential sources within the Area of Investigation including CCBs deposited at Yard 520 and the potential presence of CCBs used as fill outside of Yard 520. The chemical and physical characteristics of these CCBs will be evaluated through implementation of two previously-submitted sampling plans: the Municipal Water Service Extension (MWSE) Sampling and Analysis Plan (SAP) (ENSR, 2004) and Yard 520 SAP (ENSR, 2005b). Additional investigation activities for CCBs under the FSP include a visual inspection program to determine where suspected CCBs are present outside Yard 520; laboratory verification (both chemical and physical) will be used to determine whether the suspected CCBs are CCBs or another type of material. Based on these evaluations, the need for further information regarding the nature or extent of CCBs will be determined and follow up work implemented if necessary.

Suspected CCBs will be evaluated for both chemical and physical characteristics. Suspected CCB sampling will be conducted under the proposed MWSE SAP (ENSR, 2004a) and the proposed Yard 520 SAP (ENSR, 2005b). These SAPs were submitted to USEPA in advance of this RI/FS Work Plan. Sampling was conducted under the MWSE SAP from September through December of 2004 and will continue in 2005. The Yard 520 SAP work will be implemented upon USEPA's approval of that SAP. These two SAPs were developed primarily to characterize the chemical composition and physical characteristics of CCBs both outside of Yard 520 and at Yard 520.

The data obtained will be compared to the preliminary human health and ecological screening levels (see Appendix A of this QAPP and Volumes 5 and 6 of this RI/FS Work Plan for further detail on these screening levels). These data will be used to determine if direct contact to CCBs by either human or ecological receptors poses potential risks above USEPA target risk levels and/or whether concentrations are consistent with background levels. In addition, these data will be used in conjunction with groundwater quality data to assess the extent to which the CCBs may be contributing to the presence of boron and molybdenum, and/or other constituents above appropriate screening levels in groundwater.

After suspected CCB collection and investigation activities detailed in the SAPs (and the FSP) are completed, the need for an additional data collection activity will be considered.

In addition, geologic conditions in the south portion of the Area of Investigation will be evaluated by researching the presence or absence of a surficial aquifer in this area. According to studies conducted by the U.S. Geological Survey (USGS) (e.g., Shedlock et al., 1994), a surficial aquifer may not be present in this area, or may not be present with sufficient capacity to support a drinking water supply. If either of these is true, further investigation of CCB-related constituents in groundwater in this area is not warranted.

A6.2 Geology/Hydrogeology Characterization

The objectives of the characterization of geology and hydrology are to provide geologic information to refine the preliminary Conceptual Site Model (CSM); collect groundwater elevation data to determine groundwater flow, directions (both horizontal and vertical), and seasonal variability; characterize the hydrogeology for calculating groundwater flow and migration rates; and evaluate fate and transport of constituents in groundwater and potential impacts to surface water. The data will be collected by installing monitoring wells, logging the geologic materials encountered, collecting groundwater and surface water level measurements from wells and staff gauges on a seasonal basis, and conducting hydraulic testing (i.e., slug tests). A numerical groundwater flow model will be constructed to quantify the direction and rates of groundwater flow based on the hydrogeologic data collected. The results of these investigations will be evaluated to determine whether additional information would be needed from an additional phase of investigation.

A6.3 Groundwater – Surface Water Interactions

The interaction between groundwater and surface water will be evaluated to understand where and how much groundwater discharges/recharges to Brown Ditch, the rates of surface water flow in Brown Ditch, and seasonal changes. Data collection includes the installation of piezometers adjacent to staff gauges and measurements of flow in Brown Ditch. The groundwater and surface water flow rates will also be measured. If indicated by the results of the initial groundwater investigation, these interactions will be evaluated for additional water bodies in an additional phase of investigation.

A6.4 Nature and Extent of CCB-Derived Constituents in Groundwater and the Environment

During the RI, samples of groundwater, surface water, sediment, and CCBs will be collected and analyzed for chemical and physical characteristics. This sampling and analysis will be the basis for evaluating the presence of CCB-derived constituents in these media, to developing an understanding of the environmental chemistry of CCB-derived constituents versus constituents present in groundwater due to other potential sources, and evaluating the fate and transport of CCB-derived constituents in the environment. Depending on the information then available, an additional phase of sampling may be warranted.

Groundwater quality. Information pertaining to groundwater quality will be gathered for three key areas:

1. The area directly north of Yard 520 (labeled South Area on Figure 1-1 in the FSP) where municipal water has been provided;
2. The area northeast of Yard 520 (labeled North Area on Figure 1-1 in the FSP) where municipal water has been provided, and
3. The remainder of the Area of Investigation, primarily where there is no municipal water service.

The nature and extent of CCB-derived constituents in groundwater in these areas will be determined to the extent necessary to adequately evaluate potential current and reasonably foreseeable future risks. This includes developing an understanding of general groundwater quality conditions in these areas as well as upgradient concentrations through the sampling and analysis of groundwater. Four seasonal sampling events will be conducted for groundwater quality. Geochemical conditions affecting migration will also be evaluated. The need for any additional sampling activities will be determined after the data are evaluated.

Surface water and sediment quality. Data on surface water and sediment quality is necessary to support the evaluation of the potential human health and ecological risk associated with CCB-derived constituents in Brown Ditch. Investigations evaluating surface water and sediment quality include synoptic surface water samples and sediment samples in the various branches of Brown Ditch, and in background areas. It is anticipated that an additional investigation would be needed for further surface water and/or sediment quality only if groundwater containing CCB-derived constituents is found to discharge to other surface water bodies or wetlands, or if there is significant downstream transport of CCB-derived constituents in Brown Ditch.

A6.5 Ecological Setting/Habitat

Habitat identification and assessment will be conducted to support aquatic and terrestrial investigations, as well as to support the ERA. Initial work will focus on evaluating aquatic habitats, such as benthic and fish communities potentially found in the drainage ditches and other relevant water bodies as well as terrestrial habitats located in areas potentially affected by CCBs placed as fill.

General ecological habitats will be identified from a combination of maps, aerial photographs, previous surveys and inventories (including those provided by National Park Service) and other available literature sources. Based on this information, a preliminary ecological habitat map will be prepared, which will be ground-truthed by field reconnaissance. It is anticipated that additional investigations, consisting of an evaluation of additional wetland or terrestrial habitats, would be conducted only if necessary based on the results of the evaluation of potential sources and the groundwater investigation.

A6.6 Project/Task Summary

The number of field and QC samples that will be collected for each analytical parameter is presented in Table A-1. A summary of analytical parameters by medium is presented in Table A-2. Target compounds and analytical parameters for all matrices are presented with their respective laboratory reporting limits, method detection limits, and data quality levels in Tables A-3 (sediment), Table A-4 (suspected CCB materials) and A-5 (aqueous materials).

All data generated through field activities or through the analytical program will be reviewed internally through a tiered review process and validated prior to reporting. All of the data will be validated, either as full or limited validation except grain size distribution/bulk density. The data will be validated using USEPA guidance, Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP), and Department of Energy (DOE) guidance in conjunction with ENSR data validation protocols (provided as an attachment). The USEPA and DOE guidance, and MARLAP, will be modified to reflect any differences in analytical methodology and to incorporate the project-specific acceptance criteria defined in Section A7 of this QAPP or the method criteria, whichever is more stringent. A complete description of the data verification and data validation procedures to be used is included in Section D1 of this QAPP.

ENSR's Project QA Officer and/or Field Operations Leader will be responsible for internal technical system audits (TSAs) to verify that field sampling procedures and field sampling measurements are properly followed. Additionally, laboratory TSAs are conducted periodically by ENSR's Project QA Officer or other qualified personnel. TSAs are conducted at project start up and then periodically while the project is under way. A detailed discussion of the QA assessments that will be performed during the course of the project is provided in Section C1 of this QAPP.

Validated project data will be compared to the project measurement criteria (Relative Percent Difference (RPD) values for precision, for example). Sensitivity, representativeness, and completeness assessments will also be performed. A complete description of how validated data will be reconciled with DQOs and how the overall assessment of the data will be performed is included in Section D3 of this QAPP.

QA reports will be generated by the ENSR Project QA Officer on an as-needed basis. A complete listing and description of all documents and reports that will be generated and maintained in the project files is included in Section A9 of this QAPP.

A7 Quality Objectives and Criteria for Measurement Data

A7.1 Data Quality Objectives

The RI will consist of a sampling program and chemical analyses of groundwater, suspected CCB materials, sediment, surface water, and private well water. The field investigation is designed to provide information on the presence of CCB-derived constituents in these media, to develop an understanding of the environmental chemistry related to CCBs and to other potential sources, and to evaluate fate and transport of CCB-derived constituents in the environment. Therefore, the sampling and analysis program incorporates the following QA elements:

- A sampling program designed to obtain sufficient data to determine levels of constituents in media of interest,
- The use of sample collection and handling procedures that will ensure the representativeness and integrity of the samples,
- An analytical program designed to generate definitive data of sufficient quality and sensitivity to meet the project objectives (see Section A5.2), and
- Data deliverables that will allow verification and validation of the data and reproducibility of the reported results.

At the completion of the work outlined in the FSP, it is possible that additional information may be needed to meet RI objectives. At this time, it is not possible to anticipate what additional work may be needed, as it is dependent on the results of the activities proposed. AOC II allows for additional phases of work. If needed, a memorandum documenting the need for additional data will be submitted to USEPA, per AOC II Section VIII. 32.

The design of the RI was based on the DQO process (USEPA, 2000), a multi-step, iterative process that ensures that the type, quantity, and quality of environmental data used in decision-making is appropriate for its intended application. This process is summarized below.

DQO Step	Description
State the Problem	The disposal of CCBs at a permitted Restricted Waste Facility known as Yard 520, and the possible use of CCBs as fill in areas within the Area of Investigation outside of Yard 520 may have resulted in the release of CCB-derived constituents to the environment.
Identify the Decision	Determine whether the CCB-derived constituents in environmental media within the Area of Investigation exceed target risk levels and background currently and in the reasonably foreseeable future based on a human health risk assessment and ecological risk assessment.
Identify Inputs to the Decision	A Remedial Investigation (RI) will be conducted to collect the data necessary to support the risk assessments. As presented in the FSP, the RI includes characterization of the physical systems (geology, groundwater, habitats) and constituent concentrations in environmental medial. Specific information to be collected includes: • Constituent concentrations in suspected CCBs; • Presence/location of suspected CCBs; • Constituent concentrations in native soils; • Geology and groundwater data to evaluate directions and rates of flow and migration, including seasonality; • Recharge/discharge relationships to evaluate interactions between groundwater and surface water, including seasonality; • Constituent concentrations in groundwater, including upgradient locations; • Constituent concentrations in surface water and sediment, including reference locations; • Potential contributions from sources other than CCBs (e.g., septic systems, municipal landfills); and • Physical and geochemical conditions affecting fate and transport of CCB-derived constituents in environmental media.
Define Study Boundaries	Pines Area of Investigation, as identified in the attachment to AOC II.
Develop a Decision Rule	Constituents present above the risk-based screening levels and background will be identified as Constituents of Potential (Ecological) Concern (COPCs/COPECs). These COPCs/COPECs will be evaluated in quantitative risk assessments, as described in the HHRA and ERA Work Plans. If target risk levels and background are exceeded, then remedial actions may be proposed, together with further study to support those actions, if necessary.
Specify Decision Error Limits	A formal statistical design will not be developed for the RI/FS. However, the data will be considered acceptable if they are collected according to the RI/FS Work Plan and they meet the appropriate data validation criteria. They will then be considered appropriate to estimate exposure point concentrations (EPCs) for the risk assessments.
Optimize the Study Design	Since a formal statistical design is not being utilized, the iterative process for optimizing the sample design will not be used. As appropriate during implementation of the RI/FS, a decision rule based on a more formal statistical design may be considered in consultation with the USEPA RPM.

A7.2 Data Quality Objectives for Measurement Data

The principal objectives of the QAPP pertain to the collection of data that are sufficient to evaluate the possible presence of CCB-derived constituents in the media of interest. Therefore, the quality of the data gathered in this project can be defined in terms of the following elements: precision, accuracy, completeness, sensitivity, and representativeness. These elements are discussed below.

Precision

Precision is a measure of the degree to which two or more measurements are in agreement. Field precision is assessed through the collection and measurement of field duplicates at a rate of one duplicate per ten field samples. Precision will be measured through the calculation of relative percent difference (RPD). The objectives for field precision RPDs are 25% RPD for aqueous samples and 30% RPD for solid samples.

Precision in the laboratory is assessed through the calculation of RPD for duplicate samples, either as matrix spike/matrix spike duplicates (MS/MSDs) or as laboratory duplicates, depending on the method. Precision control limits for laboratory analyses are provided in Table A-6.

Accuracy

Accuracy is the degree of agreement between the observed value and an accepted reference or true value. Accuracy in the field is assessed through the use of equipment blanks and through the adherence to all sample handling, preservation, and holding time requirements. Field rinsate blanks will be collected at a rate of one per ten samples (or less) collected per sampling event. The objectives for equipment blanks are shown in Table A-6.

Laboratory accuracy is assessed through the analysis of MS/MSDs, laboratory control samples (LCSs), and the subsequent determination of percent recoveries (%Rs). Accuracy control limits are given in Table A-6.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. "Normal conditions" are defined as the conditions expected if the sampling plan was implemented as planned.

Field completeness is a measure of the amount of valid samples obtained during all sampling for the project. The field completeness objective is greater than 90 percent.

Laboratory completeness is a measure of the amount of valid measurements obtained from all the measurements taken in the project. The laboratory completeness objective is greater than 95 percent.

Representativeness

Representativeness is the extent to which the sampling design adequately reflects the environmental conditions of the site. The data will be considered representative of the site if all sampling and analysis activities are conducted according to the project FSP and QAPP.

Sensitivity

Sensitivity of analytical data is demonstrated by the laboratory reporting limits. The target reporting limits for the constituents to be analyzed are presented in Tables A-3 (sediment), A-4 (suspected CCB materials) and A-5 (aqueous matrices). These tables also contain the data quality levels (DQLs), which were developed using human health and ecological risk screening levels, including Maximum Contaminant Levels (MCLs), USEPA Region 9 Preliminary Remediation Goals (PRGs), USEPA RALs, Ambient Water Quality Criteria (AWQC), USEPA Region 5 Ecological Screening Levels (ESLs), Indiana Water Quality Criteria (WQC), and Oak Ridge National Laboratory (ORNL) Phytotoxicity Screening Values (Attachment A). The target reporting limits were selected in part by consideration of the DQLs to be achieved and in part by consideration of the likelihood of detectable concentrations above the DQL, as in the case of several of the metals, the actual ability of the laboratory to attain reporting limits at the DQLs and the cost-effectiveness of implementing additional, more sensitive methods in the initial stage of the investigation. The laboratories will use their most recent detection limit study results to report analytical results.

Alternative analytical methods will be evaluated if the need arises, and the QAPP will be amended, if necessary.

A8 Special Training/Certification

A8.1 Training

Field personnel will be experienced in the groundwater, suspected CCB materials, surface water, sediment, and private well water sampling techniques proposed in the FSP. Data validators will be familiar with the USEPA and DOE validation guidelines. Additionally, prior to starting work, personnel will be given instruction specific to the project, covering the following areas:

- Organization and lines of communication and authority;
- Overview of the FSP;
- QAPP requirements;
- QA/QC requirements;
- Documentation requirements; and
- Health and safety requirements.

Instructions will be provided and documented by the ENSR Project Manager, ENSR RI Task Manager, ENSR Field Operations Leader, ENSR Health and Safety Officer, and ENSR Project QA Officer.

Personnel responsible for shipping samples will also be trained in the appropriate regulations, e.g., Department of Transportation (DOT), International Civil Aviation Organization (ICAO), and International Air Transport Association (IATA).

A8.2 Certifications

Laboratories utilized for routine testing of groundwater, soils/solid matrices, surface water, sediment, and private well water will have appropriate certification for the test methods.

The RI Task Manager, Ms. Perry, is a Professional Geologist licensed to practice in Indiana. This certification will be maintained throughout the project.

A9 Documents and Records

A9.1 Project Files

The project files will be the central repository for all documents which constitute evidence relevant to sampling and analysis activities as described in this QAPP. ENSR is the custodian of the project files and will maintain the contents of the project files for the investigation, including all relevant records, reports, logs, field notebooks, pictures, subcontractor reports, and data reviews in a secured, limited access area and under custody of the ENSR Project Manager.

The project files will include at a minimum:

- Field logbooks;
- Field data and data deliverables;
- Photographs;
- Drawings;
- Sample collection logs;
- Laboratory data deliverables;
- Data validation reports;
- Data assessment reports;
- Progress reports, QA reports, interim project reports, etc.; and
- All custody documentation (COC forms, airbills, etc.).

Electronic versions of correspondence, reports, drawings, and statistical analyses will be stored in the project-specific network file. The original electronic data deliverables (EDDs) received from the laboratories, and the project database, will also be stored on the network, which is backed up daily and periodically archived off-site in accordance with ENSR Information Management policy.

Records associated with this sampling will be retained with all the project records for the duration of AOC II and for a minimum of 10 years after its termination. USEPA, NIPSCO and Brown Inc. will be notified in writing 90 days prior to destruction of the records (per AOC II Section XIII. 44.).

A9.2 Field Records

Field logbooks will provide the primary means of recording the data collection activities performed during the sampling activities. As such, entries will be described in as much detail as possible so that persons going to the field could reconstruct a particular situation without reliance on memory.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel, but will be stored in the project files when not in use. Each logbook will be identified by a project-specific document number.

Entries into the logbook will contain a variety of information. At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of visitors to the work location, and the purpose of their visit, will also be recorded in the field logbook.

Measurements made and samples collected will be recorded. All entries will be made in permanent ink, signed, and dated and no erasures or obliterations will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark and the correct entry will be made, signed and dated by the person making the correction. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location, which includes compass and distance measurements, or latitude and longitude information (e.g., obtained by using a Global Positioning System (GPS)) unit will be recorded. All equipment used to make measurements will be identified, along with the date of calibration. The coordinate system that the GPS unit displays will be recorded.

Information specific to sample collection will include:

- Sample identification number;
- Time and date of sample collection;
- Sample description (color, texture, etc.);
- Samplers' initials;
- Requested analyses;
- Depth of sample interval below ground surface (bgs) or below water surface, as measured with a steel measuring tape; and

- Location (GPS coordinates and description).

To streamline data recording, information will be recorded on standardized forms when this approach is logical. Examples of these forms are presented in the field SOPs included in Attachment B.

Descriptions of geologic materials and CCBs will be logged in accordance with Indiana guidance (IDEM, 1988).

Representative photographs of sample locations will be taken with a digital camera and the camera picture frame number, date, direction facing, and subject will also be recorded in the logbook.

COC forms will be maintained as part of the field records as described in Section B3.3.1.

A9.3 Laboratory Records and Deliverables

Laboratory data reduction procedures will be performed according to the following protocol. All information related to analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms. All entries that are not generated by an automated data system will be made neatly and legibly in permanent, waterproof ink. Information will not be erased or obliterated. Corrections will be made by drawing a single line through the error and entering the correct information adjacent to the cross-out. All changes will be initialed, dated, and, if appropriate, accompanied by a brief explanation. Unused pages or portions of pages will be crossed out to prevent future data entry. Analytical laboratory records will be reviewed by the supervisory personnel on a regular basis and by the Laboratory QA Manager periodically, to verify adherence to documentation requirements.

Data deliverables will be provided within the following turnaround time: 21 calendar days for chemical and bacteriological analyses, 28 days for radiological analyses, 21 days for physical testing, and 60 days for boron isotope ratios and tritium analyses. The laboratory will provide at least one copy of a hard copy report and one copy of an EDD. The format of the EDD is discussed in Section B11. The hard copy data package for routine chemical and radiochemical analyses will be equivalent to a Contract Laboratory Program (CLP) deliverable (i.e., consisting of all the information presented in a CLP package, including CLP-like summary forms). This information is summarized below:

- Analytical report;
- Chain of custody information;
- Notes concerning special client requests and telephone records;

- Instrument raw data;
- Standards information;
- Preparation information;
- Sample results, including units;
- Detection limits and reporting limits, including units;
- Results for MS/MSDs, method or preparation/calibration blanks, LCSs, laboratory duplicates, inductively coupled plasma (ICP) serial dilutions, and ICP interference check samples; and
- Raw data for samples and laboratory QC samples, including labeled and dated chromatograms/spectra.

Data packages for the boron isotope, bacteriological analyses, grain size distribution, bulk density tests, and tritium analyses will include, at a minimum, chain-of-custody records, sample results, QC summaries, and a narrative addressing any problems encountered.

A10 References

This QAPP was prepared using the following documents:

DOE. 1997. Evaluation of Radiochemical Data Usability.

ENSR. 2004. Municipal Water Service Extension Sampling and Analysis Plan. October 19, 2004.

ENSR. 2005a. Site Management Strategy. Pines Area of Investigation. AOC II. Docket No. V-W-'04-C-784. January 2005.

ENSR. 2005b. Yard 520 Sampling and Analysis Plan. September 2, 2005. (currently under revision)

IDEM. 1988. Technical Guidance Document, Volume 1 – Requirements for Describing Unconsolidated Deposits. Indiana Department of Environmental Management. Draft, Revised November 18, 1988.

MARLAP. 2004. Multi-Agency Radiological Laboratory Analytical Protocols Manual. July 2004.

Shedlock, R.J., D.A. Cohen, T.E. Imbrigiotta, and T.A. Thompson. 1994. Hydrogeology and Hydrochemistry of Dunes and Wetlands Along the Southern Shore of Lake Michigan, Indiana. Open File Report 92-139. U.S. Geological Survey.

USEPA. 1990. National Oil and Hazardous Substances Pollution Contingency Plan. Final Rule. 55FR8666. March 8.

USEPA. 1992. Specifications and Guidance for Contaminant-Free Sample Containers. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. December 1992.

USEPA. 1997. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. Third Edition. United States Environmental Protection Agency. May 1986, revised June 1997.

USEPA. 1998. Clarification to the 1994 Revised Interim Soil Lead Guidance for CERCLA Sites and RCRA Corrective Action Facilities. OSWER Directive 9200.4-27. August 1998.

USEPA. 2000. Guidance for the Data Quality Objectives Process, EPA QA/G-4. EPA/600/R-96/055. U.S. Environmental Protection Agency. August, 2000.

USEPA. 2000a. *Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan.* United States Environmental Protection Agency, Region 5. Revision 0. June 2000.

USEPA. 2001. *EPA Requirements for Quality Assurance Project Plans*, EPA QA/R-5. United States Environmental Protection Agency, Quality Staff. March 2001.

USEPA. 2004. *Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review*. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. October 2004.

SECTION B – MEASUREMENT/DATA ACQUISITION

B1 Sampling Process Design

The rationale for the sample design is provided in Section 2.0 of the FSP.

B2 Sampling Methods Requirements

B2.1 Field Measurements

Field measurements will be taken in conjunction with groundwater, surface water, and private well water sampling. Water level measurements will be conducted as described in Section 3.3.9 of the FSP and ENSR SOP No. 101Pines – Water Level Measurements (Attachment B). Measurement of water quality parameters during groundwater, private well water, and surface water sampling will be performed as described in FSP Sections 3.3.4, 3.3.10 and 3.3.15.1, respectively, and in the following ENSR SOPs: No. 108Pines – Field Measurement of Turbidity and No. 105Pines – Operation and Calibration of the YSI 6920 Multi-Parameter Water Monitor (Attachment B). Surveying information is presented in Sections 3.2.8 and 3.2.9 of the FSP.

B2.2 Sampling Procedures

The SOPs that will be utilized for sampling of groundwater, surface water, sediment, suspected CCB materials, and private well water are listed below and provided in Attachment B.

- ENSR SOP No. 103Pines – Surface Water and Sediment Sample Collection
- ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells
- ENSR SOP No. 106Pines – Sample Collection from Private Wells
- ENSR SOP No. 104Pines – Temporary Monitoring Well Installation and Groundwater Sampling by HydroPunch® Technology
- ENSR SOP No. 7116Pines – Subsurface Soil Sampling by GeoProbe™ Methods

B2.2.1 Groundwater Sampling

Groundwater samples will be collected in accordance with Sections 3.3.10 (groundwater purging and sampling) and 3.3.16 (HydroPunch® groundwater sampling) of the FSP.

Samples will be collected by filling each of the appropriate sample containers in rapid succession, without pre-rinsing the containers with sample. The bottle will be held under the sample stream without allowing the mouth of the bottle to come in contact with the tubing and filled completely, and the cap securely tightened. Sample collection will proceed as follows: bacteriological parameters, metals, cations/anions, and radionuclides. All dissolved constituents, if collected, will be collected after the unfiltered samples and will proceed as follows: DOC, metals, and phosphate. All sample labels will be checked for completeness, sample custody forms completed and a description of the sampling event recorded in the field notebook.

B2.2.2 Surface Water Sampling

Surface water samples will be collected in accordance with Section 3.3.15.1 of the FSP.

B2.2.3 Sediment Sampling

Sediment samples will be collected in accordance with Section 3.3.15.2 of the FSP.

B2.2.4 Private Well Sampling

Private well samples will be collected in accordance with Section 3.3.4 of the FSP.

B2.2.5 CCB Sampling

Suspected CCB materials will be collected in accordance with Section 3.3.5 of the FSP.

B2.3 Cleaning and Decontamination of Equipment/Sample Containers

Guidance on equipment decontamination is included in Attachment B, ENSR SOP No. 7600Pines. In general, equipment used will be decontaminated using the following procedure:

- Tap water rinse to remove gross contamination;

- Non-phosphate, non-borate detergent (e.g. DETERGENT8®) and water rinse;
- Tap water rinse;
- Distilled/deionized water rinse ;
- 10% nitric acid rinse;
- Distilled/deionized water rinse; and
- Air dry or wrap in aluminum foil for later use.

If sample collection tools consist entirely of disposable or dedicated implements and bowls, then no equipment decontamination is necessary for these items. See Section 3.2.7 of the FSP for information on how to dispose of these supplies.

Non-disposable and non-dedicated sampling equipment will be decontaminated prior to initial use and between samples. The effectiveness of the decontamination procedures is measured by collecting and analyzing equipment blank samples.

Sample containers will be purchased new. Specifications for these containers are addressed in Section B3.1.

B2.4 Inspection and Acceptance Requirements for Supplies/Sample Containers

For this project, critical supplies for field activities will be tracked through ENSR's system in the following manner.

Critical Supplies and Consumables	Inspection Requirements and Acceptance Criteria	Responsible Individual
Sample bottles	Visually inspected upon receipt for cracks, breakage, and cleanliness. Must be accompanied by certificate of analysis.	Field Operations Leader
Chemicals and reagents	Visually inspected for proper labeling, expiration dates, appropriate grade.	Field Operations Leader
Sampling equipment	Visually inspected for obvious defects, damage, and contamination.	Field Operations Leader
Field measurement equipment	Functional checks to ensure proper calibration and operating capacity.	Field Operations Leader

Supplies and consumables not meeting acceptance criteria will initiate the appropriate corrective action. Corrective measures may include repair or replacement of measurement equipment, and/or notification of vendor and subsequent replacement of defective or inappropriate materials. All actions will be documented in the project files.

The laboratory system of inspection and acceptance of supplies and consumables is documented in the laboratory QA Manuals. The pertinent sections of the QA Manuals are included in Attachment C.

A description of the procedures and documentation activities employed to ensure field and sampling equipment are available in working order when needed is provided in Section B6 of this QAPP.

B3 Sample Handling and Custody

B3.1 Sample Containers, Preservation, and Holding Times

Sample bottles and chemical preservatives will be provided by the laboratories, except for GTC and UMTL. The sample bottles for boron isotope ratio and tritium analyses will be purchased by ENSR from a commercial vendor. The containers will be cleaned by the manufacturer (to be determined) to meet or exceed all analyte specifications established in the latest USEPA's *Specifications and Guidance for Contaminant-Free Sample Containers* (USEPA, 1992). Certificates of analysis will be provided with each lot of containers and maintained on file to document conformance to USEPA specifications. All sample bottles and chemical preservatives provided by the laboratory will be shipped with a custody seal affixed to the outside of the cooler. The laboratory will be responsible for maintaining the certificates of analysis for the bottleware and for tracking which lot number of containers were provided with each shipment.

A summary of sample container, preservation, and holding time requirements is presented in Table B-1.

B3.2 Sample Labeling

Immediately upon collection, each sample will be labeled with an adhesive label. Samples will be assigned unique sample identifications (IDs) based on an alphanumeric code that identifies the matrix, location, date, and type of sample, as described below.

- Name of location in five digits (e.g., MW001, TP002, etc.). These location names will correspond to well/boring logs if appropriate, as well as sample locations posted on maps.

- Single letter signifying depth of sample (A, B, C, etc. for subsequent soil samples, S or D for shallow/deep monitoring wells, X if this field is not being used). The actual depth measured in the field in feet will be recorded in the field records.
- Two letters signifying the sample matrix: GW - groundwater, SW – surface water, SD - sediment, PW – private well water, and CB for known or suspected CCBs).
- Sampling date consisting of the number corresponding to the month (2 digits), day (2 digits), and year (2 digits), for example, 061204 for samples collected on June 12, 2004.
- Letter denoting the type of sample. Codes for this field include: S – sample; D – field duplicate; B – equipment rinse blank.
- Letter (F) denoting if an aqueous sample has been filtered.

No dashes will be used to separate fields. An example sample ID for the sediment sampling would be: SD011BSD070404D indicating a sediment sample collected at location SD011 on July 4, 2004. This sample is a duplicate, and collected at depth greater than another sample at the same location.

Samples designated as MS/MSDs will be noted as such in the comments field of the COC form.

The sample identification code will be recorded on the label, in the field logbook, on the COC form, and will be carried through the analytical process to reporting. An example of a sample label is included as Figure B-1.

B3.3 Custody Procedures

Custody is one of several factors that are necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in two parts: field sample collection and laboratory analysis.

A sample is considered to be under a person's custody if:

- The item is in the actual possession of a person;
- The item is in the view of the person after being in actual possession of the person;

- The item was in the actual physical possession of the person but is locked up to prevent tampering; and
- The item is in a designated and identified secure area.

B3.3.1 Field Custody Procedures

The field sampler (to be determined) is personally responsible for the care and custody of the samples until they are transferred or dispatched properly. Field procedures have been designed such that as few people as possible will handle the samples.

All sample containers will be identified by the use of adhesive sample labels (Figure B-1) which will include sample numbers, project identification (i.e., ENSR project number), date/time of collection, preservation, sampler's initials, and type of analysis. The sample numbering system is presented in Section B.3.2 of the QAPP. Sample labels will be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample label because the pen would not function in freezing weather.

Samples will be accompanied by a properly completed COC form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of samples from the sampler to another person, to the permanent laboratory, or to/from a secure storage location. ENSR SOP No. 1007Pines – Chain-of-Custody Procedures (Attachment B) includes additional information. An example COC form is presented as Figure B-2.

All sample shipments will be accompanied by the COC record identifying the contents. The original record and a copy will accompany the shipment, and a copy will be retained by the sampler and placed in the project files.

Samples will be properly packaged on ice at 4 ± 2°C, where applicable, (NO ice/cooling for boron isotope ratio and tritium samples) for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in and secured to the inside top of each sample box or cooler. Shipping containers will be locked and secured with strapping tape and custody seals for shipment to the laboratory. The custody seals will be attached to the front right and back left of the cooler and covered with clear plastic tape after being signed by field personnel. The cooler will be strapped shut with strapping tape in at least two locations. ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples (Attachment B) includes a detailed description of these procedures.

If the samples are sent by common carrier, the waybill will be retained as part of the permanent documentation. Commercial carriers are not required to sign off on the custody forms since the custody forms will be sealed inside the sample cooler and the custody seals will remain intact.

Whenever possible, samples will be transported to the laboratory the same day the samples are collected in the field by overnight carrier or laboratory courier.

B3.3.2 Laboratory Custody Procedures

Samples will be received and logged in by a designated sample custodian or his/her designee. Upon sample receipt, the sample custodian will:

- Examine the shipping containers to verify and document that the custody tape is intact;
- Examine all sample containers for damage;
- Determine if the temperature required for the requested testing program, where applicable, has been maintained during shipment and document the temperature on the COC form;
- Compare samples received against those listed on the COC;
- Verify that sample holding times have not been exceeded;
- Examine all shipping records for accuracy and completeness;
- Determine sample pH (if applicable) and record acceptability of pH on the sample receipt records;
- Sign and date the COC immediately (if shipment is accepted) and attach the waybill (if possible);
- Note any problems associated with the coolers and/or samples on the cooler receipt form and notify the Laboratory Project Manager, who will be responsible for contacting the client;
- Attach laboratory sample container labels with unique laboratory identification and test; and
- Place the samples in the proper laboratory storage.

Following receipt, samples will be logged in according to the following procedure:

- The samples will be entered into the laboratory information management system (LIMS), where applicable. At a minimum, the following information will be entered: project name or identification, unique sample numbers (both client and internal laboratory), type of sample, required tests, date and time of laboratory receipt of samples, and field ID provided by field personnel.
- The appropriate laboratory personnel will be notified of sample arrival.

- The completed COC, waybills, and any additional documentation will be placed in the project file.

Specific details of laboratory custody procedures for sample receiving, sample identification, sample control, record retention, and data purging to the final evidence file are described in the laboratory SOPs (Attachment D).

B4 Analytical Methods

Groundwater, surface water, sediment, suspected CCB materials, and private well water samples will be analyzed by CAS for the majority of analyses:

Columbia Analytical Services Inc.
1 Mustard Street, Suite 250
Rochester, NY 14609-0859 Phone: (585) 288-5380

Groundwater, sediment, and private well water samples will be analyzed by GEL for radiochemistry, boron and total uranium by ICP-MS, and physical testing parameters:

General Engineering Laboratories, LLC
2040 Savage Road
Charleston, SC 29417 Phone: (843) 556-8171

Groundwater and private well water samples will be analyzed by GTC for boron isotope ratios:

Geochemical Technologies Corp.
4855 Ward Rd., Suite 200
Wheat Ridge, CO 80033 Phone: (303) 423-8187

Groundwater and private well water samples will be analyzed by UMTL for low-level tritium:

University of Miami Tritium Laboratory
4600 Rickenbacker Cswy
Miami, FL 33149 Phone: (305) 421-4100

Groundwater and private well water samples will be analyzed by Test America Valparaiso for bacteriological parameters:

Test America Valparaiso
2400 Cumberland Drive
Valparaiso, IN 40383 Phone: (219) 464-2389

B4.1 Field Analytical Procedures

There are no field analyses associated with this project.

B4.2 Laboratory Analytical Procedures

The laboratories named above will implement the project-required SOPs. These laboratory SOPs for sample preparation and analysis are based primarily on SW-846 Third Edition, November 1986 (including all final updates through Final Update III, June 1997), Standard Methods for the Examination of Water and Wastewater, American Society for Testing and Materials (ASTM), DOE HASL300 Methods (DOE, 1982), and USEPA Methods for Chemical Analyses of Water and Wastes, except for boron isotope ratios and low-level tritium analyses. These SOPs provide sufficient detail and are specific to the analyses to be performed for this investigation. Attachment D of the QAPP contains the laboratory SOPs. Laboratory Instrument Detection Limits (IDLs) and Method Detection Limits (MDLs) are listed in Tables A-3 (sediment), A-4 (suspected CCB materials) and A-5 (aqueous). The CAS laboratory SOP for performing MDL studies is included in Attachment D-1; no SOPs for MDL studies are included for GEL, GTC, Test America Valparaiso, and UMTL as MDL studies are not applicable to the parameters being analyzed by these laboratories. A list of the laboratory SOPs included in Attachment D is provided in the Table B-2.

Table B-2 summarizes the analyte groups of interest, appropriate laboratory SOP number, and reference method for the organic (e.g., total organic carbon (TOC)/dissolved organic carbon (DOC)), inorganic analytes, and miscellaneous analytes (radionuclides, bacteriological parameters, boron isotope ratios, and low-level tritium) evaluated in the investigation.

B4.3 List of Project Target Constituents and Detection Limits

A complete listing of project target constituents and reporting limits for each analyte group listed in Table B-2 can be found in Tables A-3 (sediment), A-4 (suspected CCB materials), and A-5 (aqueous) of this QAPP.

B4.4 List of Associated Quality Control Samples

The analytical laboratory SOPs listed in Table B-2 includes a QC section which addresses the minimum QC requirements for the analysis of specific analyte groups. Section B5 of this QAPP contains a complete list of the associated QC samples for every analyte group.

B5 Quality Control

QC is the overall system of technical activities that measure the attributes and performance of a process, item or service against defined standards to verify that they meet the stated requirements. Acceptable limits of performance are defined for each QC check and sample used in the project.

B5.1 Field

QC samples will include equipment blanks, field duplicates, and MS/MSDs. These samples will be collected as described below:

B5.1.1 Equipment Blanks

Equipment blanks will be prepared by routing laboratory grade and organic free water (provided by the laboratory) through non-disposable or non-dedicated sampling equipment after equipment decontamination and before field sample collection. Equipment blanks will be collected for all aqueous and solid samples collected with non-disposable or non-dedicated equipment and will be collected at a frequency of one per 10 samples collected using a particular type of equipment. Equipment blanks will be analyzed for the same parameters as their associated samples, except that they will be limited to metals (not boron isotope ratios), sulfur, and radiochemistry (not tritium) analyses only.

B5.1.2 Field Duplicates

Field duplicates will be collected at a frequency of one field duplicate for every 10 or less investigative samples of each medium. Field duplicates will be collected by alternately filling two sets of identical sample containers from the interim container used to collect the sample. All field duplicates will be analyzed for the same parameters as their associated samples, except that they will be limited to metals, sulfur, boron isotope ratios, low-level tritium, bacteriological parameters, and radiochemistry analyses only. Whenever possible, collection of field duplicate samples will occur at locations where detectable concentrations of target analytes are expected.

B5.1.3 MS/MSDs

MS/MSD or MS/duplicate samples will be collected (when applicable to the method) at a frequency of one for every 20 or less investigative samples. For those samples designated as MS/MSDs or MS/duplicates, sufficient additional volume (based on the individual laboratory's requirements) will be collected.

B5.2 Analytical Quality Control Checks

Each laboratory has a QC program in place to ensure the reliability and validity of the analysis performed at the laboratories. All analytical procedures are documented in writing as SOPs and each SOP includes a QC section which addresses the minimum QC requirements for the procedure. The internal QC checks differ slightly for each individual procedure but in general the QC requirements may include the following:

- Method blanks
- Reagent/preparation blanks (inorganic parameters)
- Instrument blanks
- MS/MSDs
- Laboratory duplicates
- LCSs
- ICP serial dilutions
- ICP interference check samples

Table B-3 summarizes the QC for each method.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

This section describes the procedures used to verify that all instruments and equipment are maintained in sound operating condition and in working order when needed.

B6.1 Field Instrument Maintenance

The field equipment for this project includes an electronic water level indicators and water quality meters (pH, specific conductivity, dissolved oxygen [DO], temperature, turbidity, oxidation-reduction potential [ORP]). Specific preventative maintenance procedures to be followed for field equipment are based on those recommended by the manufacturer. Field instruments will be checked and calibrated daily before use and periodically throughout the day as specified in Section B8.1. The maintenance schedule and trouble-shooting procedures for field instrument are indicated in Table B-4. Critical spare parts will be kept on site to reduce potential downtime. Backup instruments and equipment will be available on site or within 1-day shipment to avoid delays in the field schedule.

B7 Laboratory Instrument Preventative Maintenance

As part of their QA manual, a routine preventative maintenance program is conducted by the laboratories to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees regularly perform routine scheduled maintenance and repair of (or coordinate with the vendor for repair of) all instruments. All maintenance that is performed is documented in the laboratories' operating record. All laboratory instruments are maintained in accordance with manufacturer's specifications. Table B-5 provides the frequency with which components of key analytical instruments will be serviced. Table B-6 provides a summary of the monitoring of laboratory equipment.

B8 Instrument/Equipment Calibration and Frequency

Calibration is required to ensure that field and laboratory analytical systems are operating correctly and functioning at the proper sensitivity to meet established detection limits.

B8.1 Field Instruments

The field instrumentation will include electronic water level indicators and water quality meters. Calibration of these instruments will be performed according to the manufacturer's instructions and the SOPs included as Attachment B. A summary of calibration procedures and frequencies is provided as Table B-7. All calibration procedures will be documented in the field records. Calibration records will include the date/time of calibration, name of the person performing the calibration, reference standard used, and the results of the calibration.

B8.2 Analytical Instrumentation

Calibration procedures for laboratory instruments will consist of initial calibrations, initial calibration verifications, and continuing calibration verification, as applicable to the method. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria, and the conditions that will require recalibration. This information is summarized in Table B-8. The SOPs are included as Attachment D.

The laboratory maintains documentation for each instrument which includes the following information: instrument identification, serial number, date of calibration, analyst, calibration solutions, and the samples associated with these calibrations, as applicable.

B9 Inspection/Acceptance of Supplies and Consumables

Inspection and acceptance procedures for field materials are discussed in Section B2.4.

The laboratory system of inspection and acceptance of supplies and consumables is documented in the laboratory QA Manuals. Pertinent sections of the laboratories' QA Manuals are included as Attachment C.

B10 Non-Direct Measurements

The suitability of use of non-direct data (historical reports, maps, literature searches, previously collected analytical data) will be evaluated and limitations potentially placed on its use. The data necessary to meet the objectives specified in Section A7 of the QAPP will be generated during the RI/FS and will come from the following sources:

- Field records (sample locations, sample observations);
- Field measurements (water quality measurements, water levels, hydraulic conductivity measurements; see Section B6.1 for further details);
- Analytical results for chemical testing of sediment, suspected CCB materials, surface water, private well water, and groundwater; and
- Ecological assessment.

The data collected under this QAPP have been designed to be of sufficient quality to meet the program objectives.

A summary of the data usability criteria and potential limitations on use in the RI/FS is presented below:

Type	Data Usability	Description
A	Qualified for use in the RI/FS	Data collected per the approved RI/FS Work Plan, maintaining consistency with approved SOPs, QAPPs, and DQOs. SOPs, QAPP, and DQOs are specifically developed to meet RI/FS objectives including use in risk assessment. Specific data uses are presented in work plans.
A	Qualified for use in the RI/FS	Data collected by others under a documented QA program. QA program, field and laboratory methods are available and equivalent to the RI/FS. Appropriate documentation is available. If all conditions are consistent with those presented in the RI/FS, then these data are qualified for uses detailed in the RI/FS.
B	Qualified for some uses in the RI/FS	Non-chemical data, such as geology, hydrology, physical data, not collected under the approved work plans, but which was collected by equally qualified personnel using methods that are no different than in the plans (e.g., USGS geology, geology from Yard 520, water levels, well construction information, etc.)

Type	Data Usability	Description
C	Qualified for limited uses in the RI/FS	Data collected by other qualified personnel, using methodologies and approaches known to be different from approved RI/FS work plans. QA programs and/or field/laboratory methods known to be different so resulting data is known to be not comparable. Not to be combined with RI/FS data. Appropriate uses to be determined by professional judgment.
D	Not suitable for use in RI/FS	Data collected by unidentified and/or unqualified personnel with little to no documentation (i.e., unidentified samplers, methodologies, locations), from locations that were not properly recorded or are now destroyed.

B11 Data Management

Data management operations include data recording, validation, transformation, transmittal, reduction, analysis, tracking, storage and retrieval.

All data will be entered into an EQuIS database system. EQuIS is a software product of Earthsoft, is widely used in the industry, and has proven to be a reliable and robust data management tool. EDDs provided by the laboratories will be in the EQUIS four-file format or in an EQuIS-compatible format that will minimize manipulation of the data.

Upon receipt from the laboratory, hard copy and EDD will be assigned a unique identifier, which allows the data to be tracked from receipt, through validation, to data loading and storage. The electronic data will be imported into the EQuIS database system concurrent with the data validation process. Data qualifiers generated during data validation will be entered manually. Definitions of all qualifiers are maintained within the database structure and electronic versions of the data validation reports are stored in the project files maintained on the network drive. Data collected in the field will also be entered into the system and integrated with laboratory data.

As data are loaded into the system, a variety of quality checks are performed to ensure data integrity. These checks include:

- Audits to ensure that laboratories reported all requested analyses;
- Checks that all analytes are consistently and correctly identified;
- Reviews to ensure that units of measurement are provided and are consistent;
- Queries to determine that any codes used in the database are documented properly;
- Reports to review sample definitions (depths, dates, locations);

- Proofing manually entered data against the hard-copy original; and
- Reports to review groupings of sampling locations and coordinate systems.

Records of the checks are maintained on file.

At a minimum, the database will contain the following fields:

Sample identifier;
Sample location;
Sample media type;
Sampling date;
Analysis date;
Laboratory analysis identifier (test method);
Analyte name;
Concentration value;
Quantitation limits;
Measurement units; and
Data qualifiers.

Data will be loaded into a "temporary" database until data validation is complete, at which time the database will be finalized. Any changes made to the database after finalization will be documented, including a description of the change, date of change, person responsible, and reason for change.

Once all data quality checks are performed, the data will be exported to a variety of formats to meet project needs. Cross-tab tables showing concentrations by sample location will be prepared. Statistical analyses will be performed as required. Data can be accessed by a variety of mapping and visualization tools.

The project database will be maintained on a secure network drive which is backed up regularly. Access to the database will be limited to authorized users and will be controlled by password access. Data will be retained in accordance with the requirements stated in Section A9.1 of this QAPP.

SECTION C – PROJECT ASSESSMENT/OVERSIGHT

C1 Assessment and Response Actions

This section identifies the number, frequency, and type of planned assessment activities that will be performed for the project.

C1.1 Assessments

C1.1.1 Field Sampling Technical System Audit

The USEPA is responsible for the external TSAs of field activities, including field sampling and measurements, for compliance of requirements specified for this project.

The Project QA Officer and/or Field Operations Leader of ENSR will be responsible for periodic internal TSAs to verify that field sampling procedures and field sampling measurements are properly followed. The TSAs will include examination of

- Field sampling records;
- Field measurement results;
- Field instrument operating and calibration records;
- Sample collection, handling, and packaging procedures;
- QA procedures;
- Chain-of-custody; and
- Sample documentation, etc.

An example of the checklist used during the internal field TSAs is included as Figure C-1. Results of internal field TSAs will be documented in the QA reports to management (Section C2).

C1.1.2 Fixed Laboratory Technical System Audits

The USEPA is responsible for the external TSAs of laboratory activities for compliance of requirements specified for this project.

System audits are performed as described in the laboratory QA manual for internal auditing or as required by accreditation authorities.

Laboratory TSAs are conducted at project start up and then periodically as the project progresses, by ENSR or another qualified party, as part of their analytical subcontractor monitoring program. The laboratory TSA includes a review of the following areas:

- QA organization and procedures;
- Personnel training and qualifications;
- Sample log-in procedures;
- Sample storage facilities;
- Analyst technique;
- Adherence to laboratory SOPs and project QAPP;
- Compliance with QA/QC objectives;
- Instrument calibration and maintenance;
- Facility security;
- Bottleware preparation;
- Waste management;
- Data archival;
- Data recording, reduction, review, and reporting; and
- Cleanliness and housekeeping.

An example of the laboratory TSA checklist is included as Figure C-2.

Preliminary results of the systems audit will be discussed with the Laboratory Director, Laboratory Project Manager, and Laboratory QA Manager. A written report that summarizes audit findings and recommends corrective actions will be prepared and submitted to the Laboratory Director for response, and to the ENSR Project Manager. The results of the audit, including resolution of any deficiencies, will be included in the QA reports to management, as described in Section C.2.

C1.1.3 Performance Evaluation Sample Assessment

Continuous performance auditing is accomplished through the regular use of LCS, matrix spike samples, duplicate samples, QC samples, proficiency testing, and through continuing calibration verification samples. Federal and State agencies may administer the proficiency testing.

Prior to the initiation of this project, the results of recent (within 6 months of the start of the program) Performance Evaluation (PE) samples analyzed by the laboratories will be reviewed and evaluated to ensure the acceptability of results for the parameters and matrices of interest. In the event that PE results are not current, not acceptable, or are not available for the target parameters, PE samples will be purchased from a commercial vendor and submitted to the laboratories for analysis prior to the start of the analytical program. PE samples are not applicable to boron isotope ratio analysis and low-level tritium analysis. The results of the PE samples analyzed by CAS, Test America Valparaiso, and GEL will be reviewed by the ENSR Project QA Officer or designee. Any deficiencies will be communicated to the ENSR Project Manager, the laboratory, and to the USEPA RPM. Corrective actions, which may include internal laboratory actions, the analysis of additional PE samples, or selection of another analytical subcontractor, will be documented in the QA reports to management (Section C2).

C1.1.4 Data Validation Technical System Audits

Data validation and verification will be performed as described in Section D.2. In summary, a subset of data received will be subjected to a full data validation. The remainder of the data will receive a limited data validation. Data will be qualified and the results of the validation will be summarized in a validation memo. Each data validation technical systems audit will be reviewed by a validator other than the one performing the validation. This review will verify that the analytical deliverable package was complete and that any missing information requested from the laboratory was supplied, that validation worksheets were filled out accurately and completely, that validation actions were consistent with the validation guidelines established for this program and/or best professional judgment, and that the validation reports and data qualifiers accurately reflect the validation actions as documented on the worksheets.

C1.1.5 Data Package Technical System Audits

Audits of analytical data packages will be conducted for 100% of the packages received as part of the data validation process (Section D.1). The review will include an evaluation of the package to ensure that (1) all required deliverables are provided, (2) each package contains the information necessary to reproduce the reported results, and (3) the QC acceptance criteria specified in the QAPP were met. Any deficiencies will be communicated to the laboratory and documented in the data validation reports.

C1.1.6 Management System Review (MSR)

On a quarterly basis, at a minimum, all projects within ENSR are reviewed. The review includes the following elements:

- Progress towards completion of the scope of work;
- Schedule versus approved plan;
- Costs and invoicing versus approved plan, including adherence to purchasing policy;
- Project task structure and associated budgets;
- Senior review assignments and documentation;
- Compliance with hard copy and electronic file management requirements;
- Client relationship development; and
- Future needs.

Documentation of the review will be maintained with the project files.

C1.2 Assessment Findings and Corrective Action Responses

Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out-of-limit QC performance that can affect data quality. Corrective action can occur during field activities, laboratory analyses, data validation, and data assessment. All corrective action proposed and implemented should be documented in the QA reports to management (Section C.2). Corrective action should only be implemented after approval by the ENSR Project Manager, or their designee.

C1.2.1 Field Corrective Action

Corrective action in the field may be needed when the sample frequency is changed (i.e., more/fewer samples, sample locations other than those specified in the QAPP, etc.), or when sampling procedures and/or field analytical procedures require modification, etc. due to unexpected conditions. The field team may identify the need for corrective action. The Field Operations Leader will approve the corrective action and notify the Project Manager. The Project Manager will approve the corrective measure. The Field Operations Leader will ensure that the field team implements the corrective action. Refer to ENSR No. SOP 100Pines - Field Change Order Procedures (Attachment B) for further discussion of field corrective actions.

Corrective action resulting from internal field audits will be implemented immediately if data may be adversely affected due to unapproved or improper use of approved methods. The QA auditor will identify deficiencies and recommend corrective action to the Field Operations Leader. The Field Operations Leader and field team will perform implementation of corrective actions. Corrective action will be documented in QA reports to the project management team (Section C2).

Corrective actions will be implemented and documented in the field record book. Documentation will include:

- A description of the circumstances that initiated the corrective action;
- The action taken in response;
- The final resolution;
- Any necessary approvals; and
- Effectiveness of corrective action.

No staff member will initiate corrective action without prior communication of findings through the proper channels.

If at any time a corrective action issue is identified which directly impacts the project DQOs, the USEPA RPM will be notified.

C1.2.2 Laboratory Corrective Action

Corrective action in the laboratory is specified in laboratory SOPs, as applicable, and may occur prior to, during, and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or analysis. Following consultation with laboratory analysts and supervisory personnel, it may be necessary for the Laboratory QA Manager to approve the implementation of corrective action. If the nonconformance causes project objectives not to be achieved, the ENSR Project QA Officer will be notified, who will in turn notify the ENSR Project Manager, who will communicate with the Respondent Project Managers and other members of the project team, as necessary. The USEPA RPM will also be notified in those cases where the nonconformance affects the achievement of the project DQOs.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action files, and in the narrative data report generated by the laboratory. If the corrective action does not rectify the situation, the laboratory will contact the ENSR Project QA Officer, who will determine the action to be taken and inform the appropriate personnel.

C1.2.3 Corrective Action During Data Validation and Data Assessment

The need for corrective action may be identified during either data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory. These actions are dependent upon the ability to mobilize the field team and whether the data to be collected are necessary to meet the required QA objectives. If the data validator or data assessor identifies a corrective action situation that impacts the achievement of the project objectives, the ENSR Project Manager will be responsible for informing the appropriate personnel, including the USEPA RPM.

C2 Reports to Management

QA reports will be prepared by the ENSR Project QA Officer and submitted on an as-needed basis to the ENSR Project Manager. QA reports will document any problems identified during the sampling and analysis programs and the corrective measures taken in response. The QA reports will include:

- All results of field and laboratory audits;
- Problems noted and actions taken during data validation and assessment; and

- Significant QA/QC problems, recommended corrective actions, and the outcome of corrective actions.

A summary of QA issues, audit findings, and significant nonconformances will be included in the status reports to the USEPA. A complete listing and description of all documents and reports that will be maintained in the project files is included in Section A9 of this QAPP.

SECTION D – DATA VALIDATION AND USABILITY

This element details the QA activities that will be performed to ensure that the collected data are scientifically defensible, properly documented, of known quality, and meet project objectives. Two steps are completed to ensure that project data quality needs are met:

- Data Verification/Validation
- Data Usability Assessment

D1 Data Review, Verification, and Validation

All data generated through field activities or through the analytical program, will be reduced and validated prior to reporting. No data will be disseminated until it has been subjected to the procedures summarized below.

D1.1 Field Data Review

The field data verification includes verification of sampling design, sample collection procedures and sample handling. Field data will be reviewed daily by the Field Operations Leader to ensure that the records are complete, accurate, and legible and to verify that the sampling procedures are in accordance with the protocols specified in the FSP and QAPP (refer to Section D2.1 for the specific elements reviewed).

D1.2 Internal Laboratory Review

Prior to the release of any data from the laboratory, the data will be reviewed and approved by laboratory personnel. The review will consist of a tiered approach (Section D2.2) that will include reviews by the person performing the work, by a qualified peer, and by supervisory and/or QA personnel.

D1.3 Validation of Analytical Data

Analytical data validation includes the verification and validation of analytical procedures, QC, calibration, and data reduction. Validation of the laboratory deliverables will be performed by ENSR. One hundred percent of the analytical data will receive validation, either as full or limited validation.

Ten percent of the routine chemical and radiochemical data will be subjected to full validation and the remainder will receive limited validation. The boron isotope ratio data, bacteriological data, and the low-level tritium data will undergo a limited validation. The grain size distribution and bulk density data will not be validated. The ten percent of data selected for full validation will be representative of all matrices and analyses. It is expected that full validation will occur early in the validation process to identify any potential systematic problem and then will be performed periodically as needed.

For full validation, the data will be reviewed for the following, where applicable to the method (as identified in Table A-6):

- Completeness of deliverable;
- Technical holding times and sample preservation;
- Laboratory and field blank contamination;
- Field and laboratory duplicates;
- MS/MSD recoveries and RPDs;
- Post-digestion spike recoveries;
- LCS recoveries;
- Initial and continuing calibrations;
- ICP serial dilution results;
- ICP interference check sample results; and
- Calculation and transcription verifications (i.e., verifying summary data against raw data).

Limited validation will be performed using information presented on summary forms and will include the following, as applicable to the analyses:

- Completeness of deliverable;
- Technical holding times and sample preservation;
- Laboratory and field blank contamination;
- Field and laboratory duplicates;
- MS/MSD recoveries and RPDs; and
- LCS recoveries.

The discovery of significant anomalies or discrepancies during validation using the summary forms may result in an in-depth review of the raw data and the incorporation of additional review elements into the validation of all data.

D2 Validation and Verification Methods

D2.1 Field Data Verification

Field records will be reviewed by the Field Operations Leader to ensure that:

- Logbooks and standardized forms have been filled out completely and that the information recorded accurately reflects the activities that were performed.
- Records are legible and in accordance with good recordkeeping practices, i.e., entries are signed and dated, data are not obliterated, changes are initialed, dated, and explained.
- Sample collection, handling, preservation, storage, and shipping procedures were conducted in accordance with the protocols described in the FSP and QAPP, and that any deviations were documented and approved by the appropriate personnel.

D2.2 Laboratory Data Verification

Prior to being released as final, laboratory data will proceed through a tiered review process. Data verification starts with the analyst who performs a 100 percent review of the data to ensure the work was done correctly the first time. The data reduction and initial verification process must ensure that:

- Sample preparation and analysis information is correct and complete;
- Analytical results are correct and complete;
- Reporting limits are correct;
- The appropriate SOPs have been followed and are identified in the project records;
- Proper documentation procedures have been followed; and
- All nonconformances have been documented.

Following the completion of the initial verification by the analyst performing the data reduction, a systematic check of the data will be performed by an experienced peer or supervisor. This check will be performed to ensure that initial review has been completed correctly and thoroughly and will include a review of:

- Adherence to the requested analytical method SOP;
- Correctness of numerical input when computer programs are used (checked randomly);
- Correct identification and quantitation of constituents with appropriate qualifiers;
- Numerical correctness of calculations and formulas (checked randomly);
- Acceptability of QC data;
- Documentation that instruments were operating according to method specifications (calibrations, performance checks, etc.);
- Documentation of dilution factors, standard concentrations, etc.; and
- Sample holding time assessment.

A third-level review will be performed by the Laboratory Project Manager before results are submitted to clients. This review serves to verify the completeness of the data report and to ensure that project requirements are met for the analyses performed. A narrative to accompany the final report will be prepared by the Laboratory Project Manager.

D2.3 Validation of Analytical Deliverables

Validation will be performed by ENSR as described in Section D.1.3 of the QAPP using the “Contract Laboratory Program National Functional Guidelines for Inorganic Data Review” (USEPA, 2004), “Evaluation of Radiochemical Data Usability (DOE, 1997), and “Multi-Agency Radiological Laboratory Analytical Protocols Manual” (MARLAP, 2004) in conjunction with ENSR data validation protocols. Examples of the ENSR data validation protocols are provided in Attachment E. These guidelines will be modified to reflect any differences in analytical methodology and to incorporate the project-specific acceptance criteria defined in Section A.7 of this QAPP or the method criteria, whichever is more stringent.

Upon completion of the validation, a report will be prepared. This report will summarize the samples reviewed, elements reviewed, any nonconformances with the established criteria, and validation actions (including application of data qualifiers). Data qualifiers will be consistent with the USEPA, DOE, and/or MARLAP guidelines as shown below:

- J - The result is an estimated quantity; the associated numerical value is the approximate concentration of the analyte in the sample.
- J+ - the result is an estimated quantity, but the result may be biased high (this qualifier will be used only for metals data).
- J- – The result is an estimated quantity, but the result may be biased low (this qualifier will be used only for metals data).
- UJ - The analyte was not detected above the sample reporting limit; and the reporting limit is approximate.
- U - The analyte was analyzed for, but was not detected above the sample reporting limit.
- R – The data are unusable. The sample result is rejected due to serious deficiencies. The presence or absence of the analyte cannot be verified.
- B – The result may be a false positive (totally attributed to blank contamination) (this qualifier will be used for radiochemical data only).
- JB – The result may be biased high (partially attributed to blank contamination) (this qualifier will be used for radiochemical data only).

D2.4 Verification during Data Management

Data provided electronically used to facilitate data handling will be verified against the hard copy data report during data validation.

D3 Usability/Reconciliation with Data Quality Objectives

This element describes how the verified/validated project data will reconcile with the project DQOs, how data quality issues will be addressed and how limitations on the use of the data will be reported and handled. The purpose of this section is to indicate the methods by which it will be ensured that the data collected for this investigation falls in line with the DQOs as described in Sections A.7 of this QAPP. To meet these DQOs, a combination of statistical procedures and qualitative evaluations will be used to check the quality of the data. These procedures will be used by the laboratory, in generating the data, and by the Data Validator, in the evaluation of the data for ultimate use in accordance with the RI/FS Work Plan.

The data generated must meet the data user's needs as defined in the project DQOs in Sections A.7 of this QAPP. The primary objectives for assessing the usability of the data are to ensure (1) data are representative of conditions in the Area of Investigation; (2) data meet the project reporting limit requirements; and (3) data are of the quality needed in order to meet the overall objective of the RI/FS.

Results for QC samples, including field and laboratory blanks, spikes, and duplicates will be evaluated using the equations described below to determine the validity and usability of the data. In addition, the data will be reviewed for indications of interferences to results caused by sample matrices, contamination during sampling, contamination in the laboratory, and sample preservation and storage anomalies (i.e., sample holding time or analytical instrument problems).

Data will be qualified for precision and accuracy by the Data Validator. The Data Validator will apply the standard data validation qualifiers to data to indicate the level of uncertainty in the associated result. In general, data that are left unqualified, data qualified “U” (non-detected), data qualified “J (+/-)” (detected as an estimated result), “B” (false positive), “JB” (partial false positive). and data qualified “UJ” (non-detected at an estimated detection reporting limit) are considered valid and usable for project objectives. Data that are qualified “R” (rejected), due to severe exceedances of QC requirements, will be considered invalid and unusable for making project decisions.

D3.1 Comparison to Measurement Criteria

D3.1.1 Precision Assessment

The RPD, as a measure of variability between the matrix spike and matrix spike duplicate or sample and matrix duplicate (laboratory duplicates), and field duplicates, will be calculated to compare to precision and representativeness DQOs. The RPD of duplicate measurements is calculated according to the following formula:

$$\text{RPD} = \frac{|\text{Result in Sample 1 - Result in Sample 2}|}{\text{Average (Result in Sample 1 and Result in Sample 2)}} \times 100$$

where:

Sample 1 = Initial sample or spiked sample result

Sample 2 = Duplicate sample or duplicate spiked sample result

In the event of precision results that do not meet the measurement performance criteria established for this project the results will be inspected to determine if the reduced precision can be attributed to sampling techniques (field duplicates) or sample contamination (field and laboratory blanks). If precision has been determined to be affected by sampling or contamination the data users must decide how to use data near the project action limits that may be affected. Data of reduced precision might be usable with appropriate acknowledgement of the uncertainty associated with results that are near action levels.

D3.1.2 Accuracy Assessment

Accuracy, as a measure of bias, will be evaluated based on the percent recoveries (%Rs) of the matrix spike sample, matrix spike duplicate sample, LCS, and initial and continuing calibration check samples. These QC results will be compared to the project measurement performance criteria for accuracy.

The increase in concentration of the analyte observed in the spiked sample, due to the addition of a known quantity of the analyte, compared to the reported value of the same analyte in the unspiked sample determines the %R.

Percent recoveries for spiked samples and QC are determined using the following equation:

$$\%R = \frac{\text{Result in Spiked Sample - Result in Original Unspiked Sample}}{\text{Known Amount of Spike Added}} \times 100$$

Percent recoveries for LCS are determined using the following equation:

$$\%R = \frac{\text{Result for constituent in LCS}}{\text{Verified amount of constituent in LCS from vendor information}} \times 100$$

Additionally, field and laboratory blanks will be used to evaluate whether field or laboratory procedures represent a possible source of contamination in the samples. Unmonitored contamination can allow false positive results to be reported and treated as true sample components when, in fact, they are not. This type of error will adversely affect the accuracy of the reported results. Several types of blanks, including field blanks, method blanks, and instrument blanks, will be used in this project as described in Section B.5.B.

Specific DQOs for blanks have been defined for this program in Sections B.5.B. In general, the procedure for assessing blank samples for potential contamination is as follows.

- Tabulate blank constituent results.
- Identify blank samples for which constituents are reported above the method detection limits.

- If no constituents are detected above the instrument or method detection limits in any blanks, the associated data are reported unqualified and no blank actions are taken.
- If constituents are detected above instrument or method detection limits in the blanks, the associated sample constituent results may be qualified during data validation. This qualification may result in the negation of results at raised reporting limits due to blank actions.

Thus potential false results will be reported with elevated reported limits. These elevated limits will be recognized in the data available for the end user. Bias that does not meet the limits of the measurement criteria objectives will be indicated by the results of LCS, MS, and calibration analyses. Bias indicated by these measurement criteria objectives will need to be evaluated to determine the effect on the use of the data. High bias on nondetect results, results that are well below action levels, or well over action levels may have little effect on the use of the data. Low bias for results that are well below the action levels or well over the action levels may have little effect on the use of the data. For results near the action levels with a high or low bias or indeterminate bias, the data will need to be reviewed carefully to establish if the data is usable for the intended purposes. Sample reanalysis, analysis of archived material, and/or recollection of the sample may be appropriate depending on criticalness of the missing data, logistical constraints, cost, and schedule.

D3.1.3 Completeness Assessment

Completeness is the ratio of the number of valid sample results to the total number of results planned for collection. The goal of this program is to generate valid, usable data. However, in environmental sampling and analysis, some data may be lost due to sampling location logistics, field or laboratory errors, or matrix effects that may cause the rejection of results for some constituents. The overall completeness goal of collection of valid data is 90% for the field and 95% for analytical data. The Data Validator will assess the completeness of the overall data generation against the project goals of a minimum of 90% as valid and usable results. Valid and usable results are defined as those that are not rejected during validation (e.g., due to severe holding time or spike recovery noncompliance) or during the overall assessment (e.g., improper sampling technique). Following completion of the sampling, analysis, and data validation, the percent completeness will be calculated and compared to the project objectives stated in Section A7.2 using the following equation.

$$\% \text{ Completeness} = \frac{\text{Number of valid/usable results obtained}}{\text{Number of valid/usable results planned}} \times 100$$

If this goal is not met, data gaps may exist that will require evaluation to determine the effect on the intended use of the data. Sample reanalysis, analysis of archived material, and/or recollection of the sample may be appropriate depending on criticalness of the missing data logistical constraints, cost, and schedule.

D3.1.4 Sensitivity

Sensitivity is evaluated by verifying that laboratory reporting limits meet the target reporting limits stated in Tables A-3 and A-4. The failure to calibrate with a standard at the laboratory reporting limit or the presence of excessive dilutions may result in elevated detection limits. The effect of these elevated limits will need to be reviewed in light of the historical data and project action levels to determine if adequate information is available to satisfy the DQOs.

D3.1.5 Representativeness

Representativeness expresses the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary.

Measures to Ensure Representativeness of Field Data

Representativeness is dependent upon the proper design of the sampling program and will be satisfied by ensuring that the FSP and QAPP are followed and that proper sampling techniques are used. In designing the sampling program, media of interest have been specified.

Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory is ensured by using the proper analytical procedures, appropriate methods, meeting sample holding times, and analyzing and assessing field duplicate samples. The sampling network was designed to provide data representative of the Area of Investigation. During development of this network, consideration was given to past facility processes, existing analytical data, physical setting and processes, and media of interest. The rationale of the sampling network is discussed in detail in Section 2.0 of the FSP.

D3.2 Overall Assessment of Environmental Data

Data assessment will involve data evaluation and usability to determine if the data collected are of the appropriate quality, quantity, and representativeness to the project decision. This evaluation will be performed by the Project Manager in concert with other users of the data. The QC results associated with each analytical parameter for each matrix type will be compared to the objectives presented in this QAPP. Data generated in association with QC results meeting these objectives and/or the data validation criteria will be considered usable. Data that does not meet the objectives and/or the data validation criteria might still be usable. This assessment may require various statistical procedures to establish outliers, correlations between data sets, adequate sampling location coverage, etc., in order to assess the effect of qualification or rejection of data. The effect of the qualification of data or loss of data deemed unacceptable for use, for whatever reason, will be discussed and decisions made on corrective action for potential data gaps.

Figure A-1 Project Organization Chart

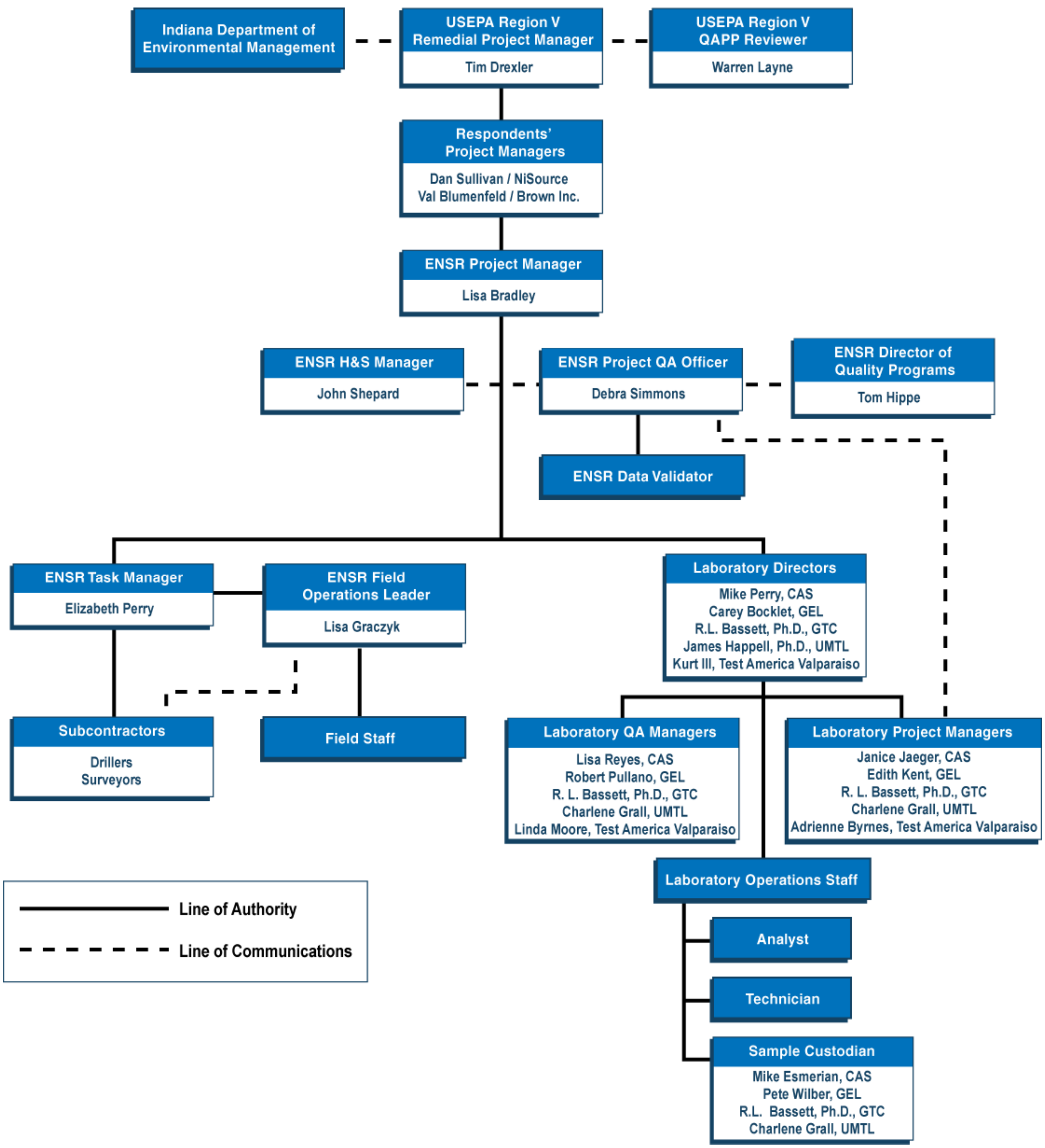
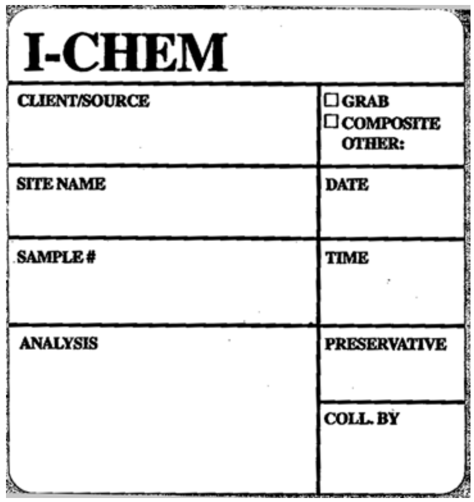


Figure B-1 Example of Sample Label



I-CHEM

CLIENT/SOURCE	☐ GRAB ☐ COMPOSITE OTHER:
SITE NAME	DATE
SAMPLE #	TIME
ANALYSIS	PRESERVATIVE COLL. BY

Figure B-2 Example Chain-of-Custody Record

ENSR | AECOM

CHAIN OF CUSTODY RECORD

Page ____ of ____

Client/Project Name:	Project Location:	Analysis Requested
Project Number:	Field Logbook No.:	
Sampler (Print Name)/(Affiliation):	Chain of Custody Tape Nos.:	
Signature:	Send Results/Report to: / TAT:	

Container Type
P – Plastic
A – Amber Glass
G – Clear Glass
V – VOA Vial
O – Other
E – Encore

Preservation
1 – HCl, 4°
2 – H2SO4, 4°
3 – HNO3, 4°
4 – NaOH, 4°
5 – NaOH/ZnAc, 4°
6 – Na2S2O3, 4°
7 – 4°

Matrix Codes:
DW – Drinking Water
WW – Wastewater
GW – Groundwater
SW – Surface Water
ST – Storm Water
W – Water
S – Soil
SL – Sludge
SD – Sediment
SO – Solid
A – Air
L – Liquid
P – Product

Field Sample No./Identification	Date	Time	COMP	GRAB	Sample Container (Size/Mat'l)	Matrix	Preserv.	Field Filtered											Lab I.D.	Remarks

Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Analytical Laboratory (Destination):
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	
Relinquished by: (Print Name)/(Affiliation) Signature:	Date: Time:	Received by: (Print Name)/(Affiliation) Signature:	Date: Time:	Sample Shipped Via: UPS FedEx Courier Other / Temp blank: Yes No

Serial No.______

Figure C-1 Example of Internal Field TSA Checklist

Project: **Site Location:** **Auditor:**	
1. Was project-specific training held?	
2. Are copies of project plan (FSP, QAPP) on site and available to personnel?	
3. Are samples being collected in accordance with the project plan?	
4. Do the numbers and locations of samples conform to the project plan?	
5. Are sample locations staked or otherwise marked?	
6. Are samples labeled in accordance with the project plan?	
7. Is equipment decontamination in accordance with the project plan?	
8. Is field instrumentation being operated and calibrated in accordance with the project plan?	
9. Are samples being preserved and containerized in accordance with the project plan?	
10. Are QC samples in accordance with the types, collection procedures, and frequencies specified in the project plan?	
11. Are chain-of-custody procedures and documents in conformance with the project plan?	
12. Are field records complete, accurate, up-to-date, and in conformance to good recordkeeping procedures?	
13. Are modifications to the project plan being communicated, approved, and documented appropriately?	
Additional Comments:	
Auditor:	**Date:**

Figure C-2 Example of Laboratory Audit Checklist

Project: **Facility Location:** **Auditor:**	
Is there a written QA Program Plan/Manual?	
Is there a designated QA Officer?	
Are facilities and equipment adequate to perform the analyses of interest?	
Review procedures and engineering controls for minimizing cross contamination.	
Review most recent interlaboratory PE sample results and recent Agency audits.	
Review SOP system. Review techniques for conformance to approved SOPs.	
Are personnel qualified and trained? Is there a formal training program and are records of training and proficiency maintained?	
Is there a designated sample custodian? Is there a sample inspection checklist? Are sample log-in procedures defined in an SOP?	
Is the laboratory area secure?	
Review internal chain-of-custody procedures.	
Are instruments operated and calibrated in accordance with SOPs? Are records of calibration maintained?	
Is equipment maintained according to written protocols? Are routine and non-routine maintenance procedures documented?	
Are samples being analyzed in conformance to the cited methods?	
Are QC samples and checks being performed at the frequencies stated in the cited methods?	
Are records complete, accurate, up-to-date, and in conformance to good recordkeeping procedures?	
How are project-specific requirements communicated to the bench level?	
Review data reduction, review, and reporting processes.	
Review data archival process (paper and electronic).	
Review audit and corrective action program.	
Additional Comments:	
Auditor:	**Date:**

Table A-1 Sample Summary

MATRIX	NO. OF LOCATIONS (SAMPLES)	FIELD PARAMETERS	ANALYTICAL PARAMETERS	EQUIPMENT BLANKS[3]	FIELD DUPS.	MS/ MSDs
Groundwater	28 wells (1 sample per monitoring well)	pH, specific conductivity, DO, temperature, turbidity, ORP	Metals,[1] strontium, ammonia, bicarbonate, chloride, fluoride, nitrate, ortho-phosphate, silica, sulfate, sulfide, surfactants (MBAS), DOC, boron isotope ratios, bacteriological parameters[6]	3	3	2 pairs
	11 wells (1 sample per select monitoring wells)	pH, specific conductivity, DO, temperature, turbidity, ORP	Lithium, U-234, U-235, U-238, Ra-226, Ra-228, total uranium, low-level tritium (5 out of 11 wells)	1	2	1 pair
	5 locations (4 samples per HydroPunch® location)	pH, specific conductivity, DO, temperature, turbidity, ORP	Boron, molybdenum	-	2	1 pair
Private Well Water	11 wells (1 sample per well)	pH, specific conductivity, DO, temperature, turbidity, ORP	Metals[1], strontium, ammonia, bicarbonate, chloride, fluoride, nitrate, ortho-phosphate, sulfate, sulfide, surfactants (MBAS), DOC, silica, low-level tritium, boron isotope ratios, bacteriological parameters[6]	-	2	1 pair
Sediment (0-6 inches)	20 locations (1 sample per location)	None	Metals[1], sulfur, TOC, grain size, bulk density	2	2	1 pair
Sediment (6-12 inches)	6 locations (1 sample per location)[5]	None	Metals[1], sulfur, TOC, grain size, bulk density	1	1	1 pair
Suspected CCBs	3 locations (1 sample per location)	None	Metals[4], sulfur	1	1	1 pair
Surface Water	24 locations (1 sample per location)	pH, specific conductivity, DO, temperature, turbidity, ORP	Metals[1,2], strontium, ammonia, bicarbonate, chloride, fluoride, nitrate ortho-phosphate, silica, sulfate, sulfide, DOC, hardness, TSS	-	3	2 pairs

[1]Aluminum, arsenic, barium, boron, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silicon, sodium, thallium, vanadium, and zinc.
[2] Arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc will be collected as filtered and unfiltered samples.
[3] Equipment rinsate blanks will be collected when non-disposable or non-dedicated equipment is used. Refer to Section B.5.1.1 for the relevant analytes.
[4]Aluminum, arsenic, antimony, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, thallium, vanadium, and zinc.
[5]All samples will be retained by the laboratory for later analyses, if required (see Volume 6, Ecological Risk Assessment Work Plan).
[6]Total coliform and Escherichia Coli.
Note: Sample numbers are estimates; actual numbers will be based on final sample numbers and field conditions.

Table A-2 Laboratory Parameters by Sample Medium

Parameter	Media				
	Sediment	**Groundwater**	**Surface Water**	**Private Well Water**	**Suspected CCB**
Ammonia		X	X	X	
Bicarbonate		X	X	X	
Bulk Density	X				
Chloride		X	X	X	
DOC		X	X	X	
Fluoride		X	X	X	
Grain Size	X				
U-234, U-235, U-238		X			
Ra-226 and Ra-228		X			
Hardness			X		
Lithium		X			
Metals[1]	X	X[2]	X	X	X[3]
Nitrate		X	X	X	
Percent Moisture	X				X
Ortho-Phosphate		X	X	X	
Silica		X	X	X	
Strontium		X	X	X	
Sulfate		X	X	X	
Sulfide		X	X	X	
Sulfur	X				X
Surfactants (MBAS)		X		X	
TOC	X				
TSS			X		
Tritium		X		X	
Boron isotope ratios		X		X	
Total Uranium (by ICP-MS)		X			
Boron (by ICP-MS)		X	X	X	
Total Coliform/ Escherichia Coli		X		X	

[1]Aluminum, arsenic, barium, boron, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, silicon, selenium, sodium, thallium, vanadium, and zinc.

[2] Select groundwater samples (those from HydroPunch® locations) will be analyzed only for boron and molybdenum.

[3] Antimony, beryllium, cobalt, mercury, and silver will also be analyzed.

Table A-3 Target Analytes, Reporting Limits, and Data Quality Levels for Sediment

Parameter	CAS No.	IDL/MDL	RL	Ecological DQL	Human Health DQL	Selected DQL
Metals (mg/kg)						
Aluminum	7429-90-5	5.1	10	25,500	76,000	25,500
Arsenic	7440-38-2	0.25	1	9.79	0.39	0.39
Barium	7440-39-3	0.56	2	NS	5,400	5,400
Boron	7440-42-8	1.68	20	NS	16,000	16,000
Cadmium	7440-43-9	0.07	0.5	0.99	37	0.99
Calcium	7440-70-2	3.76	50	NS	NS	NS
Chromium (total)	7440-47-3	0.06	1	43.4	210	43.4
Copper	7440-50-8	0.19	2	31.6	3,100	31.6
Iron	7439-89-6	0.05	10	20,000	NS	20,000
Lead	7439-92-1	0.16	0.5	35.8	400	35.8
Magnesium	7439-95-4	3.81	50	NS	NS	NS
Manganese	7439-96-5	0.06	1	460	1,800	460
Molybdenum	7439-97-7	0.17	1	NS	390	390
Nickel	7440-02-0	0.19	4	16	1,600	16
Potassium	7440-09-7	7.52	200	NS	NS	NS
Selenium	7782-49-2	0.43	0.5	0.29	390	0.29
Silicon	7631-86-9	6.49	100	NS	NS	NS
Sodium	7440-23-5	5.31	50	NS	NS	NS
Strontium	7440-24-6	10	10	NS	NS	NS
Thallium	7440-28-0	0.13	1	NS	5.2	5.2
Uranium (total) by ICP-MS[1]	7440-61-1	0.05	0.05	NS	NS	NS
Vanadium	7440-62-2	0.15	5	50	78	50
Zinc	7440-66-6	0.06	2	121	23,000	121
Other (mg/kg)						
Sulfur	7704-34-9	12.19	20	NS	NS	NS
TOC	C-012	62.5	300	NS	NS	NS
Grain Size Distribution	-	NA	NA	NS	NS	NS
Bulk Density	-	NA	NA	NS	NS	NS

Notes:
[1] Represents the sum of U-235 and U-238
Laboratory RLs and IDLs/MDLs are on an "as-received" basis. Actual dry weight limits will vary based on percent moisture of the samples. IDLs/MDLs are updated periodically; the current IDLs/MDLs at the time of analyses will be used. IDLs will be utilized for metals; MDLs for the remaining parameters.
Arsenic and selenium will be reported as nondetect at the IDL.
CAS – Chemical Abstracts Service
DQL – Data Quality Level. Refer to Attachment A for sources. Refer to Section A.7.2 for a discussion of the sensitivity of the proposed methods and achievement of the DQLs.
IDL – Instrument Detection Limit
MDL – Method Detection Limit
NA – Not Applicable
NS – None Specified
RL – Reporting Limit

Table A-4 Target Analytes, Reporting Limits, and Data Quality Levels for Suspected CCB Materials

Parameter	CAS No.	IDL/MDL	RL	Ecological DQL	Human Health DQL	Selected DQL
Metals (mg/kg)						
Aluminum	7429-90-5	5.1	10	50	76,000	50
Antimony	7440-36-0	0.29	6	0.29	31	0.29
Arsenic	7440-38-2	0.25	1	5.7	0.39	0.39
Barium	7440-39-3	0.56	2	330	5,400	330
Beryllium	7440-41-7	0.01	0.5	36	150	36
Boron	7440-42-8	1.68	20	0.5	16,000	0.5
Cadmium	7440-43-9	0.07	0.5	0.38	37	0.38
Calcium	7440-70-2	3.76	50	NS	NS	NS
Chromium (total)	7440-47-3	0.06	1	0.4	210	0.4
Cobalt	7440-48-4	0.12	5	13	900	13
Copper	7440-50-8	0.19	2	5.4	3,100	5.4
Iron	7439-89-6	0.05	10	NS	NS	NS
Lead	7439-92-1	0.16	0.5	16	400	16
Magnesium	7439-95-4	3.81	50	NS	NS	NS
Manganese	7439-96-5	0.06	1	500	1,800	500
Mercury	7439-97-6	0.003	0.03	0.1	23	0.1
Molybdenum	7439-97-7	0.17	1.0	2	390	2
Nickel	7440-02-0	0.19	4	30	1,600	30
Potassium	7440-09-7	7.52	200	NS	NS	NS
Selenium	7782-49-2	0.43	0.5	0.028	390	0.028
Silicon	7631-86-9	6.49	100	NS	NS	NS
Silver	7440-22-4	0.071	1	4.0	390	4.0
Sodium	7440-23-5	5.31	50	NS	NS	NS
Thallium	7440-28-0	0.13	1	0.057	5.2	0.057
Vanadium	7440-62-2	0.15	5	1.6	78	1.6
Zinc	7440-66-6	0.06	2	6.6	23,000	6.6
Other (mg/kg)						
Sulfur	7704-34-9	12.19	20	NS	NS	NS

Notes:
Laboratory RLs and IDLs/MDLs are on an “as-received” basis. Actual dry weight limits will vary based on percent moisture of the samples. IDLs/MDLs are updated periodically; the current IDLs/MDLs at the time of analyses will be used. IDLs will be utilized for metals; MDLs for the remaining parameters.
Antimony, arsenic, boron, cadmium, chromium, selenium, thallium, and vanadium will be reported as nondetect at the IDL.
CAS – Chemical Abstracts Service
DQL – Data Quality Level. Refer to Attachment A for sources. Refer to Section A.7.2 for a discussion of the sensitivity of the proposed methods and achievement of the DQLs.
IDL – Instrument Detection Limit
MDL – Method Detection Limit
NS – None Specified
RL – Reporting Limit

Table A-5 Target Analytes, Reporting Limits, and Data Quality Levels for Groundwater, Surface Water, and Private Well Water (Page 1 of 2)

Parameter	CAS No.	IDL/MDL/ MDA[1]	RL	Ecological DQL	Human Health DQL	Selected DQL
Metals (μg/L)						
Aluminum[3]	7429-90-5	50.9	100	87	36,000	87
Arsenic[3]	7440-38-2	2.5	10	150	0.045	0.045
Barium[3]	7440-39-3	5.6	20	4	2000	4
Boron (by ICP-MS)	7440-42-8	4	15	1.6	900	1.6
Cadmium[3]	7440-43-9	0.7	5	0.25	5	0.25
Calcium	7440-70-2	37.6	500	NS	NS	NS
Chromium (total)	7440-47-3	0.6	10	11	100	11
Copper	7440-50-8	1.9	20	8.96	1330	8.96
Iron	7439-89-6	5.2	100	1000	NS	1000
Lead	7439-92-1	1.6	5	2.5	15	2.5
Lithium	7439-93-2	23.9	100	NS	NS	NS
Magnesium	7439-95-4	38.1	500	NS	NS	NS
Manganese	7439-96-5	0.6	10	120	880	120
Molybdenum	7439-97-7	1.7	10	370	10	10
Nickel	7440-02-0	1.9	40	52	500	52
Potassium	7440-09-7	75.2	2000	NS	NS	NS
Selenium[3]	7782-49-2	4.3	5	4.61	50	4.61
Silicon	7440-21-3	64.9	1000	NS	NS	NS
Sodium	7440-23-5	53.1	500	NS	NS	NS
Strontium	7440-24-6	8.42	100	1500	22,000	1500
Thallium[3]	7440-28-0	1.48	10	12	2	2
Uranium (total) by ICP-MS[4]	7440-61-1	0.05	0.2	2.6	7.3	2.6
Vanadium[3]	7440-62-2	1.5	50	20	36	20
Zinc	7440-66-6	0.6	20	118	3000	118

Table A-5 Target Analytes, Reporting Limits, and Data Quality Levels for Groundwater, Surface Water, and Private Well Water (Page 2 of 2)

Parameter	CAS No.	IDL/ MDL/ MDA[1]	RL	Ecological DQL[2]	Human Health DQL[2]	Selected DQL[2]
Other (mg/L)						
Ammonia	7664-41-7	0.010	0.05	NS	NS	NS
Bicarbonate	71-52-3	0.75	2.0	NS	NS	NS
Chloride	16887-00-6	0.05	0.20	NS	NS	NS
DOC	763-69-9	0.09	1.0	NS	NS	NS
Fluoride	16984-48-8	0.03	0.10	NS	NS	NS
Nitrate	14797-55-8	0.04	0.05	NS	NS	NS
Ortho-Phosphate	14265-44-2	0.00078	0.002	NS	NS	NS
Silica	7631-86-9	0.0012	0.01	NS	NS	NS
Sulfate	14808-79-8	0.132	0.20	NS	NS	NS
Sulfide	18496-25-8	0.977	1.00	NS	NS	NS
Surfactants (MBAS)	--	0.007	0.02	NS	NS	NS
TSS	C-009	NA	1.0	NS	NS	NS
Hardness	--	NA	NA	NS	NS	NS
Boron isotope ratios (no units)	NA	NA[5]	NA[5]	NS	NS	NS
Tritium (Tu) (pCi/L)	10028-17-8	0.1 (0.32)	0.1 (0.32)	NS	NS	NS
Total Coliform/ Escherichia Coli (no units)	NA	NA[7]	NA[7]	NS	NS	NS
Radionuclides (pCi/L)						
Radium-226	13982-63-3	1	1	NS	0.00082	0.00082
Radium-228	15262-20-1	1	1	NS	0.0458	0.0458
Uranium-234$_6$	13966-29-5	0.6	0.6	NS	0.674	0.674
Uranium-235[6]	15117-96-1	0.6	0.6	NS	0.684	0.684
Uranium-238[6]	7440-61-1	0.6	0.6	NS	0.744	0.744

Notes:
[1]Laboratory IDLs/MDLs are updated periodically; the current IDLs and MDLs will be used at the time of analyses.
[2]DQL – Data Quality Level. Refer to Attachment A for sources. Refer to Section A.7.2 for a discussion of the sensitivity of the proposed methods and achievement of the DQLs.
[3]Aluminum, arsenic, barium, boron, cadmium, selenium, thallium, and vanadium will be reported as nondetect at the IDL/MDL
[4]Represents the sum of U-235 and U-238..
[5]For boron isotope ratio analysis, a precision of <1/mL is require to meet project objectives.
[6]Uranium will be reported as U-233/234, U-235/236, and U-238.
[7]For Total Coliform/Escherichia Coli the test is absent or present.
IDL – Instrument Detection Limit (metals)
MDL – Method Detection Limit
MDA – Minimum Detectable Activity (radionuclides only). MDAs are estimated; actual MDAs are sample-specific.
NA – Not Applicable
NS – None Specified
RL – Reporting Limit

Table A-6 Quality Control Performance Criteria (page 1 of 2)

Compound	Field and Lab Blanks	Field Duplicate %RPD[1]	LCS % R		Matrix Spike % R		Duplicate % RPD [2]
			Water	Solid	Water	Solid	
Metals by SW-846 6010B/6020/7000 series							
Aluminum	<RL	25% (aqueous); 30% (solid)	80-120	C of A	75-125	75-125	20
Antimony	<RL		80-120	C of A	75-125	75-125	20
Arsenic	<RL		80-120	C of A	75-125	75-125	20
Barium	<RL		80-120	C of A	75-125	75-125	20
Beryllium	<RL		80-120	C of A	75-125	75-125	20
Boron[3]	<RL		80-120	C of A	75-125	75-125	20
Cadmium	<RL		80-120	C of A	75-125	75-125	20
Calcium	<RL		80-120	C of A	75-125	75-125	20
Chromium	<RL		80-120	C of A	75-125	75-125	20
Cobalt	<RL		80-120	C of A	75-125	75-125	20
Copper	<RL		80-120	C of A	75-125	75-125	20
Iron	<RL		80-120	C of A	75-125	75-125	20
Lead	<RL		80-120	C of A	75-125	75-125	20
Lithium	<RL		80-120	NA	75-125	NA	20
Magnesium	<RL		80-120	C of A	75-125	75-125	20
Manganese	<RL		80-120	C of A	75-125	75-125	20
Mercury	<RL		80-120	C of A	75-125	75-125	20
Molybdenum	<RL		80-120	C of A	75-125	75-125	20
Nickel	<RL		80-120	C of A	75-125	75-125	20
Potassium	<RL		80-120	C of A	75-125	75-125	20
Selenium	<RL		80-120	C of A	75-125	75-125	20
Silicon	<RL		80-120	C of A	75-125	75-125	20
Silver	<RL		80-120	C of A	75-125	75-125	20
Sodium	<RL		80-120	C of A	75-125	75-125	20
Strontium	<RL		80-120	NA	75-125	NA	20
Thallium	<RL		80-120	C of A	75-125	75-125	20
Uranium (total) (by Method 6020)	<RL		80-120	80-120	75-125	75-125	20%
Vanadium	<RL		80-120	C of A	75-125	75-125	20
Zinc	<RL		80-120	C of A	75-125	75-125	20
Other							
Ammonia	<RL	NA	90-110	NA	64-122	NA	20%
Bicarbonate	<RL	NA	92-109	NA	85-119	NA	20%
Chloride	<RL	NA	90-110	NA	74-119	NA	20%
DOC	<RL	NA	80-114	NA	63-133	NA	20%
Fluoride	<RL	NA	90-110	NA	66-137	NA	20%
Nitrate	<RL	NA	90-110	NA	86-107	NA	20%
Ortho-Phosphate	<RL	NA	90-110	NA	76-117	NA	20%
Ra-226	<MDA	25%	75-125	NA	75-125	NA	20%
Ra-228	<MDA	25%	75-125	NA	75-125	NA	20%
Silica	<RL	25%	90-118	NA	81-122	NA	20%
Sulfate	<RL	NA	90-110	NA	69-120	NA	20%
Sulfur	< RL	30%	NA	80-120	NA	70-130	NA

Table A-6 Quality Control Performance Criteria (page 2 of 2)

Compound	Field and Lab Blanks	Field Duplicate %RPD[1]	LCS % R		Matrix Spike % R		Duplicate % RPD [2]
			Water	Solid	Water	Solid	
Sulfide	<RL	NA	44-102	NA	30-101	NA	20%
Surfactants (MBAS)	< RL	NA	58-122	NA	NA	NA	20%
TOC	<RL	NA	NA	79-116	NA	28-160	30%
TSS	<RL	NA	80-120	NA	NA	NA	20%
U-234, U-235, U238	<MDA	25%	75-125	NA	75-125	NA	20%
Grain Size Distribution	NA	NA	NA	NA	NA	NA	NA
Bulk Density	NA	NA	NA	NA	NA	NA	25%
Hardness	NA	NA	NA	NA	NA	NA	NA
Boron isotope ratio	NA	25%	NA	NA	NA	NA	Diff by >1.5/ml then re-run or flag data
Tritium	<RL	25%	NA	NA	NA	NA	$\underline{+}$3.5%
Total Coliform/Escherichia Coli	Not Present	NA	NA	NA	NA	NA	Both present or both absent

[1] RPD criteria when results are less than 5x RL = 100%
[2] RPD criteria applies to both aqueous and solid samples
[3]Boron criteria are the same for Methods 6010 and 6020.
MDA – Minimum Detectable Activity
NA – Not Applicable
C of A – The limits on the Certificate of Analysis supplied by the vendor will be utilized
RPD – Relative Percent Difference
% - Percent Recovery
LCS – Laboratory Control Sample
RL – Reporting Limit

Table B-1 Summary of Sample Container, Preservation, and Holding Time Requirements

Parameter	Container [1, 2]	Preservation	Holding Time [3]
Aqueous			
Metals[4] and hardness	500-ml plastic bottle	$HN0_3$ to pH < 2. Cool 4°C	180 days
Metals[4], dissolved	500-ml plastic bottle	$HN0_3$ to pH < 2. Filter in field prior to preservation. Cool 4°C	180 days
Sulfate, chloride, fluoride, nitrate	500-ml plastic bottle	Cool 4°C	28 days (48 hours for nitrate)
Orthophosphate	500-ml plastic bottle	Cool 4°C	48 hours
Ammonia	Plastic or glass bottle[5]	H_2S0_4 to pH < 2. Cool 4°C	28 days
Bicarbonate	Plastic bottle	Cool 4°C	14 days
Sulfide	500-ml plastic bottle	2N Zinc acetate & 2-3 pellets sodium hydroxide. Cool 4°C	7 days
TSS	Plastic or glass bottle[5]	Cool 4°C	7 days
DOC	40-ml glass bottle[5]	Cool 4°C	28 days
Silica	Plastic bottle	Cool 4º C	28 days
Surfactants (MBAS)	1L plastic bottle	Cool 4°C	48 hours
Ra-226, Ra-228, U-234, U-235, U-236	1gallon plastic cubitainer	1N $HN0_3$ to pH ≤ 2.	6 months[7]
Boron isotope ratios	1 gallon plastic cubitainer	None	6 months[7]
Tritium	1 liter polyethylene bottles (HDPE)	None	6 months[7]
Boron and Total Uranium by ICP-MS	250-ml plastic bottle	HNO_3 to pH<2. Cool 4°c	180 days
Solid			
Metals[4]	Wide-mouth 500-mL plastic jar[6]	Cool 4°C	180 days; 28 days for mercury
Boron and Total Uranium by ICP-MS	Wide-mouth 500 mL plastic jar[6]	Cool 4°C	180 days
Sulfur	Wide-mouth 500-mL plastic jar	Cool 4°C	28 days
Grain Size Distribution	Wide-mouth glass	Cool 4º C	None
Bulk Density	500-ml plastic or glass jar[5]	Cool 4°C	None
TOC	Glass jar[5]	Cool 4°C	14 days
Total coliform/ Escherichia Coli	Sterile 125 ml bottles[8]	Cool 4°C Sodium thiosulfate	6 – 24 hours

[1] Additional volume will be collected for MS/MSD samples.
[2] Laboratory may provide alternate containers as long as the containers meet the requirements of the method and allow the collection of sufficient volume to perform the analyses.
[3] Holding time begins from date and time of sample collection.
[4] Refer to Table A-2 for list of specific analytes by media.
[5] Glass containers will be placed in zipper-lock bags prior to shipping.
[6] If glass containers are used, they must be certified clean for boron and silicon.
[7] Contractual holding time rather than technical holding time.
[8] The sample container is a non-fluorescent, transparent, sterilized vessel supplied by Test America Valparaiso.
DOC – Dissolved Organic Carbon
TOC - Total Organic Carbon
TSS – Total Suspended Solids

Table B-2 Analytical Methodologies (Page 1 of 2)

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent Method Number[3]
Aqueous Samples		
Metals (except as noted below)	MET-3010A Rev. 4 MET-6010Bpines Rev. 1	USEPA SW-846 Method 3010A USEPA SW-846 Method 6010B
Thallium	MET-3020A, Rev. 3 MET-GFAA, Rev. 3	USEPA SW-846 Method 3020A USEPA SW-846 Method 7841
Sulfate, chloride, fluoride, nitrate	GEN-300.0 Rev. 3	EPA 300.0
Ortho-Phosphate	GEN-opo4	EPA 365.1
Hardness	GEN-2340B	SM 2340B (calculation)
Surfactants (MBAS)	GEN-425.1 Rev. 3	EPA 425.1
Ammonia	GEN-350.1 Rev. 3	EPA 350.1
Bicarbonate	GEN-310.1 Rev. 3	EPA 310.1
DOC	GEN-415.1/9060 Rev. 5	EPA 415.1
Ra-226	GL-RAD-A-008, Rev. 8	EPA 903.1
Ra-228	GL-RAD-A-009, Rev. 11	EPA 904.0
Sulfide	GEN-9030B/9034 Rev. 1	SW-8469030B/9034
Silica	GEN-370.1 Rev. 1	EPA 370.1
TSS	GEN-160.2 Rev.3	EPA 160.2
U-234, U-235, U-238	GL-RAD-A-011, Rev. 14	DOE HASL 300
Boron, Total Uranium (by ICP-MS)	GL-MA-E-008 Rev. 11 GL-MS-E-014 Rev. 9	USEPA SW-846 Method 3010A USEPA SW-846 Method 6020
Total Coliform/ Escherichia Coli	VM1-9223B, Rev. 2	Standard Method 9223B, Version 13
Solid Samples		
Metals	MET-3050Pines Rev.0 MET-6010Bpines Rev. 1	USEPA SW-846 Method 3050B USEPA SW-846 Method 6010B
Mercury	MET-7471Apines	USEPA SW-846 Method 7471A
Thallium	MET-3050B, Rev. 3 MET-GFAA, Rev. 3	USEPA SW-846 Method 3050B USEPA SW-846 Method 7841
TOC	GEN-TOCLK/9060 Rev. 2	USEPA Lloyd Kahn Method
Sulfur	MET-ICSPines Rev. 0 GEN-300Pines Rev. 0	EPA 300.0
Grain Size	GL-GC-E-119 Rev. 0	ASTM D422-63

Table B-2 Analytical Methodologies (Page 2 of 2)

Analyte Group[1]	Laboratory SOP Number[2]	Equivalent Method Number[3]
Boron Isotope ratio	TIMS SOP (no number)	None
Tritium	Tritium Procedures and Standards for Enrichment and Low-Level proportional counting (no numbers)	None
Bulk Density	GL-GC-E-064 Rev. 3	ASTM D5057
Boron, Total Uranium (by ICP-MS)	GL-MA-E-009 Rev. 12 GL-MA-E-014 Rev. 9	USEPA SW-846 Method 3050B USEPA SW-846 Method 6020

[1]See Tables A-3, A-4, and A-5 for the compounds in each analyte group.
[2]The version of the SOP that is current at the time of sample analysis will be utilized. Any modification to the approved SOP will require USEPA notification and concurrence.
[3]References: refer to Section A10.
ICP-MS – Inductively Coupled Plasma-Mass Spectrometry
SOP – Standard Operating Procedure
DOC – Dissolved Organic Carbon
TOC – Total Organic Carbon
TSS – Total Suspended Solids

Table B-3 Analytical Quality Control Checks (Page 1 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Metals 6010B	Reagent/prep/ ICBK blanks	One per preparation batch	No analytes above RL	Repreparation/reanalysis of entire prep batch
	MS samples	One per preparation batch	75-125% R	Analyze post-digestion spike
	Duplicate samples	One per preparation batch	RPD < 20	Check analytical system, flag results
	LCS	One per preparation batch	Vendor limits	Repreparation/reanalysis of entire prep batch
	Dilution test	One per preparation batch	Within 10% of original sample results	Flag results
	Interference check	Beginning of each analytical run	20% of true values	Recalibrate and reanalyze any sample with interfering elements
Metals 6020	Reagent/Prep/ICB/ CCB blanks	1 per analytical batch of 20 samples or less, CCBs every 10 samples in analytical run	No analytes above RL	Repreparation/reanalysis of entire prep batch
	MS Samples	1 per analytical batch of 20 samples or less	75-125% R	Analyze post digestion spike
	MS Duplicate Samples	1 per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	1 per analytical batch of 20 samples or less	80-120% R	Repreparation/reanalysis of entire prep batch
	Dilution Test	1 per analytical batch of 20 samples or less	10% (results >4 x RL)	Flag results
	Interference check	Beginning of each analytical run	80-120% R	Recalibrate, reanalyze any sample with interfering elements
Mercury 7471A	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	75-125%R (lab limits)	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	ERA Vendor listed limits.	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 2 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Thallium 7841	Reagent/prep blanks	One per analytical batch of 20 samples or less	Not detected above MRL	Repreparation/reanalysis of entire batch
	MS samples	One per analytical batch of 20 samples or less	75-125%R (lab limits)	Repreparation/reanalysis of entire batch
	Duplicate samples	One per analytical batch of 20 samples or less	RPD <20	Check analytical system, flag results
	LCS	One per analytical batch of 20 samples or less	ERA Vendor listed limits.	Repreparation/reanalysis of entire batch
Sulfate, chloride, fluoride, nitrate 300.0	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	Control limits listed in Table A-5.	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	Control limits listed in Table A-5.	Repreparation/reanalysis of entire batch
Sulfur 300Pines	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	Control limits listed in Table A-5.	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	Control limits listed in Table A-5.	Repreparation/reanalysis of entire batch
Sulfide 9034	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	30-101 %R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	44-102 %R	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 3 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Ammonia 350.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch of 10	64-122 %R	Check LCS, flag results
	Duplicate samples	One per preparation batch of 10	RPD <20	Check analytical system, flag results
	CCBK	Every 10 samples and ending	Not detected above RL	Check analytical system, reanalyze associated samples
	LCS	One per preparation batch	90-110 %R	Repreparation/reanalysis of entire batch
Bicarbonate 310.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	85-119 %R	Repeat analysis, flag results
	CCBK	Every 10 samples and ending	Not detected above RL	Check analytical system, reanalyze associated samples
	Duplicate samples	One per preparation batch of 10	RPD <20	Repeat analysis, flag results
	LCS	One per preparation batch	92-109 %R	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 4 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
TSS 160.2	Reagent/prep blanks	One per preparation batch of 10	Not detected above RL	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch of 10	RPD <20	Repeat analysis, flag results
	LCS	One per preparation batch	80-120 %R	Repreparation/reanalysis of entire batch
DOC 415.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	63-133 %R	Check LCS, flag results
	CCBK	Every 10 and ending	Not detected above RL	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch of 10	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	80-114 %R	Repreparation/reanalysis of entire batch
Ra-226 903.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	75-125% R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 5 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Ra-228 904.0	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	Tracer	Added to all samples	25-125% R	Re-extract and reanalyze samples with tracer %Rs outside criteria
	MS samples	One per preparation batch	75-125% R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch
Isotopic Uranium DOE HASL 300	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	Tracer	Added to all samples	25-125% R	Re-extract and reanalyze samples with tracer %Rs outside criteria
	MS samples	One per preparation batch	75-125% R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	75-125% R	Repreparation/reanalysis of entire batch
Surfactants (MBAs) 425.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch	RPD < 20	Check analytical system, flag results
	LCS	One per preparation batch	58-122% R	Repreparation/reanalysis of entire batch

Table B-3 Analytical Quality Control Checks (Page 6 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
Silica 370.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per batch of 10	81-122 %R	Check LCS, flag results
	CCBK	Every 10 and ending	Not detected above RL	Repreparation/reanalysis of entire batch
	Duplicate samples	One per preparation batch of 10	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	90-118 %R	Repreparation/reanalysis of entire batch
Ortho-Phosphate 365.1	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	76-117 %R	Check LCS, flag results
	Duplicate samples	One per preparation batch	RPD <20	Check analytical system, flag results
	LCS	One per preparation batch	90-110 %R	Repreparation/reanalysis of entire batch
Grain Size Distribution ASTM D422-63	NA	NA	NA	NA
Bulk Density ASTM D5057	Duplicate Samples	One every 10 samples	RPD < 25	Check analysis system, flag results
Hardness SM 2340B	NA (calculation method)	NA	NA	NA

Table B-3 Analytical Quality Control Checks (Page 7 of 7)

Parameter/ Method	QC Check	Frequencies[1]	Control Limits	Laboratory Corrective Actions
TOC Lloyd Kahn	Reagent/prep blanks	One per preparation batch	Not detected above RL	Repreparation/reanalysis of entire batch
	MS samples	One per preparation batch	75-125% R	Check LCS, flag results
	CCBK	Every 10 samples and ending	Not detected above RL	Check analytical system, reanalyze associated samples
	Duplicate samples	One per preparation batch	RPD < 30	Check analytical system, flag results
	LCS	One per preparation batch	80-120% R	Repreparation/reanalysis of entire batch
Boron isotope ratio TIMS	Standard	2 per batch of 10	Used to determine correction	
	Duplicate samples	One per 10 samples	Diff < 1.5/mL	Re-run sample flag results
	NBS Standard	One per batch	Determines machine bias and accuracy	Record data
Tritium Enrichment and low-level proportional counting	Blanks	One per batch	<RL	Repreparation/reanalysis of entire batch and/or flag results
	Duplicate samples	One per 10 samples or batch	$\pm$ 3.5%	Re-run or flag results
	Standards	One per analytical batch	$\pm$ 3.5% of calculated value	Re-run samples or flag results
Total Coliform/ Excherichia Coli	Readycult Test	Monthly	<u>Bottle should be green and fluorescent</u>	Readycult reagent not used and discarded
	Sterility Check	Each commercial lot and batch of laboratory prepared material	<u>Clean-Absent for Total Coliform</u>	Do not use the commercial lot and/or laboratory prepared batch of materials

1 = Preparation Batch defined as maximum of 20 field samples of a similar matrix unless otherwise specified.
MS/MSD = Matrix Spike/Matrix Spike Duplicate
RL = Reporting Limit
%R = Percent Recovery
LCS = Laboratory Control Sample
RPD = Relative Percent Difference
MDA = Minimum Detectable Activity
CCBK = Continuing Calibration Blank
ICBK = Initial Calibration Blank

Table B-4 Maintenance Procedures and Schedule for Field Instruments

Instrument	Maintenance Procedures/Schedule	Spare Parts in Stock
Water Quality Meters	DO probe- Change KCl and Teflon membrane prior to deployment or when (1) bubbles are visible under the membrane, (2) significant deposits of dried electrolyte are visible on the membrane or o-ring, (3) probe gives unstable readings or malfunctions. Conductivity/temperature probe – Clean openings to conductivity probe prior to initial use. pH probe – Clean probe with clean water and clean cloth if deposits or contaminants are visible on probe. All meters – Check the battery daily and recharge if necessary.	Battery charger Reagents Extra probes, cables
Turbidity Meter	Clean the outside of all sample and standard tubes prior to placing in the instrument with a clean, lint-free absorbent wipe until the tube is dry and smudge-free. Check the battery daily and recharge if necessary.	Batteries Reference standards Sample tubes Clean lint-free wipes
Electronic water-level indicator	Check instrument operation by submerging in a bucket of water. Check the battery daily and recharge if necessary.	Battery charger

Table B-5 Maintenance Procedures and Schedule for Analytical Instruments (Page 1 of 3)

Instrument	Spare Parts	Activity	Frequency
ICP (SW-846 Method 6010B)	Gases	Check gases	Daily
	O-rings	Check argon tank pressure	Daily
	Tubing	Check aspiration tubing	Daily
		Check vacuum pump gauge	Daily
		Check cooling water system	Daily
		Check nebulizer	Daily
		Check capillary tubing	Daily
		Check peristaltic pump tubing	Daily
		Check high voltage switch	Daily
		Check exhaust screens	Daily
		Check torch, glassware, aerosol injector tube, bonnet	Daily
		Clean plasma torch assembly	Monthly or as needed
		Clean nebulizer and drain chamber	Monthly or as needed
		Clean filters	Monthly or as needed
		Replace tubing	Monthly or as needed
		Check o-rings	Monthly or as needed
ICP (SW-846 Method 6020)		Clean nebulizer tip after use	As needed
		Replace peripump sample introduction tubing	As needed
		Change pump hoses on drain systems	As needed
		Check drain waste collection containers, and empty as necessary	As needed
		Check Neslab water level and add water if required	As needed
		Clean/replace interface cones	As needed
		Clean/replace nebulizer	As needed
		Clean/replace torch	As needed
		Check/replace water filter	As needed
		Change oil in interface rotary pump (or as needed).	Quarterly
		Clean ion lenses 4-6 months (or as needed).	Quarterly
		Clean air filters	6 months
		Change pump oil in backing rotary pump)	12 months
		Evaluate/replace EM (electron multiplier)	
CVAAS (SW-846 Method 7471A)	Tubing	Check tubing/change tubing	As needed
	Lamps	Check gas pressure	As needed
		Clean optical tubes	As needed
		Check filter membrane for moisture	As needed
GFAAS (SW-846 Method 7841)	Tubing	Check tubing/change tubing	As needed
	Lamps	Check gas pressure	As needed
		Clean optical tubes	As needed
		Check filter membrane for moisture	As needed

Table B-5 Maintenance Procedures and Schedule for Analytical Instruments (Page 2 of 3)

Instrument	Spare Parts	Activity	Frequency
pH probe Bicarbonate Method (310.1)	Electrode filling solution	Change filling of Orion glass bulb pH probe Clean electrode with mild soap and water solution	Weekly Weekly
Ion Chromatograph Method (300.0 and 300Pines)		Rinse IC pump and valves Lubricate pump	Weekly Every 6 months
Gas Evolution Apparatus Sulfide Method (9030B/9034)		Leak-check connections	Daily
Sample and disposable cups Ammonia Method (350.1)		Rinse with D.I. water and dry Change pump tubes	Daily As needed
Lachat Quickem IV Silica Method (370.1) and Ortho-Phosphate Method (365.1)		Rinse with D.I. water and dry Change pump tubes	Daily As needed
Vacuum pump TSS Method (160.2)		Add oil	As needed
DOC Analyzer DOC Method (415.1)		Check D.I water flask to be sure it is full and being purged Leak-check system	Daily As needed
Gamma Spectrometer (Ra-228)		Energy and FWHM calibration Efficiency calibration Instrument Check Background Liquid Nitrogen Fill Software Backups Filter Cleaning	Annual Annual Daily Weekly Weekly Monthly Quarterly
Gas Flow Proportional Counter (Ra-228)		Efficiency calibration Daily Background and efficiency Weekly Background Software Backup Sample Changer Cleaning Gas Supply Change	Annual Daily Weekly Monthly Periodically At or near depletion of gas supply
Alpha Spectrometer (Isotopic U)		Pulser Check Efficiency Calibration (Energy, FWHM, efficiency) Background Check Software Backup Vacuum Pump Oil Changed Filter Cleaning	Daily Monthly Weekly Monthly Semi-annually Quarterly
Spectrophotometer Surfactants (MBAs) (425.1)		Calibrate	Every 6 months

Table B-5 Maintenance Procedures and Schedule for Analytical Instruments (Page 3 of 3)

Instrument	Spare Parts	Activity	Frequency
Hydrometer Grain Size Distribution ASTM D422-63		NA	NA
TOC Analyzer with Boat Module TOC Method (Lloyd Kahn)	Gases	Replace Cu/Sn scrubber if clogged Replace gas cylinder if necessary Leak-check carrier gases Replace boat module's combustion tube and cobalt oxide catalyst	Daily Weekly Weekly Every 2 weeks
Incubators		Professionally Serviced	Annually
Autoclave	Temperature gauge	Professionally Serviced and calibrated	Annually
	Sterilization temperature	Check with a maximum registering thermometer (MRT) 90 - 200°C	Weekly
	Automatic timing mechanism	Check timer with stop watch	Monthly
	Heat sensitive tapes, spore strips/spore ampoules	Check availability since need for each sterilization	Each sterilization

Table B-6 Laboratory Equipment Monitoring

Equipment Type	Activity	Frequency
Ovens	Temperature monitoring Electronics serviced	Daily As needed
Refrigerators	Temperature monitoring Refrigerant system and electronics serviced	Twice daily As needed
Balances	Calibration Manufacturer cleaning and servicing	Daily or before use Annually
High-purity water system	Conductance monitoring	Daily

Table B-7 Field Instrument Calibration (Page 1 of 2)

Parameter	Calibration Frequency	Calibration Standards	Acceptance Criteria
pH	Initial: Each time instrument is turned on or if the instrument gives erratic results	Two reference buffers which bracket expected sample values	Within ≤0.1 pH unit of true value
	Check: Every 15 samples and at the end of the day	pH 7 reference buffer (difference source as initial calibration buffer)	Within ≤0.1 pH unit of true value or instrument will be recalibrated
Specific conductivity	Initial: Each time instrument is turned on or if the instrument gives erratic results	One reference standard close to expected sample values	Within 5% of true value
	Check: Every 15 samples and at the end of the day	Initial reference standard	Within 5% of true value or instrument will be recalibrated
DO	Initial: Each time the instrument is turned on or if the instrument gives erratic results	Moist air	Within 5% of true value (based on altitude and temperature)
	Check: Every 15 samples and at the end of the day	Moist air	Within 5% of true value or instrument will be recalibrated
Turbidity	Initial: Each time the instrument is turned on or if the instrument gives erratic results	Two standards, 0.0 NTU and 100 NTU	Within 10% of true value
	Check: Every 15 samples or if instrument gives erratic results	100 NTU standard	Within 10% of true value or instrument will be recalibrated
Temperature	Initial: Factory calibrated annually; no field calibration required.	NA	NA
	Check: Prior to use in field	NIST-traceable thermometer	Within 10% of NIST-traceable thermometer or instrument will be replaced

Table B-7 Field Instrument Calibration (Page 2 of 2)

Parameter	Calibration Frequency	Calibration Standards	Acceptance Criteria
ORP	Initial: Each time the instrument is turned on or if the instrument gives erratic results	Two standards which bracket expected sample concentrations	Within 169-177 mV or instrument will be replaced.
	Check: Every 15 samples and at the end of the day	Reference standard from a different source than initial standard.	Within 169-177 mV or instrument will be replaced.
Water level	Initial: Prior to program use.	Steel tape or another water level indicator	Within 10% or instrument will be replaced
	Check: At end of program or if instrument erratic results	Steel tape or another water level indicator	Within 10% or instrument will be replaced

Table B-8 Analytical Instrument Calibration (Page 1 of 5)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
ICP Metals by SW-846 6010B	Initial: Daily	Initial: Per manufacturer's instructions. Minimum of one standard and calibration blank and instrument blank.	Initial: Highest standard within 10% of true value. % RSD 20 < RL
	Continuing: Every 10 samples	Mid-level of each meta and instrument blank	±10% of true value % RSD 20 < RL
	Ending	Mid-level of each metal and instrument blank	±10% of true value % RSD 20 < RL
Boron, Uranium by ICP-MS. SW-846 6020	Instrument tune: Daily	Per manufacturer: tune solution of 10 ug/L, Be, Mg , Co, In, Pb	Manufacturer's recommended tune criteria as specified in SOP.
	Initial: Daily	Initial per manufacturer's instructions – minimum of one calibration standard, one calibration blank and interference check standards ICS-A, ICS-AB	+10% true value % RSD 20 <RL +20% recovery
	Continuing: every 10 samples	One calibration standard and one calibration blank	+10% true value % RSD 20 <RL
	Ending	If required: run CRDL , ICS-A and ICS-AB interference check standards, one calibration standard, one calibration blank	+20% recovery +10% true value % RSD 20 <RL
Mercury by SW-846 7471A	Initial: Daily and/or after recalibration	Six standards plus blank Initial Mid-Level standard	r > 0.995 ICV ±10% of true value
	Continuing: Every 10 samples	Mid-level standard	±10% of true value of original prepared standard
	Ending	Mid-level standard	±10% of original prepared standard

Table B-8 Analytical Instrument Calibration (Page 2 of 5)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Thallium by SW-846 7841	Initial: Daily and/or after recalibration	Initial: Minimum of three standards and calibration blank.	Initial: r > 0.995 ICV ≤ 10% D
	Continuing: One per 10 analyses	Mid-level	±10% of true value of original prepared standard
	Ending	Mid-level standard	±10% of true value of original prepared standard
Sulfate, chloride, fluoride, nitrate by Method 300.0	Initial: Every 6 months or as needed	3 standards plus blank	R ≥ 0.995 ±10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±10% of true value Not > RL
	Ending	Mid-level plus blank	±10% of true value Not > RL
Sulfur	Initial: Every 6 months or as needed	3 standards plus blank	R ≥ 0.995 ±10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±10% of true value **Not > RL**
	Ending	Mid-level plus blank	±10% of true value **Not > RL**
Bicarbonate by Method 310.1	Initial: Daily	Mid-level plus blank	±10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±10% of true value Not > RL
	Ending	Mid-level plus blank	±10% of true value Not > RL
Sulfide by SW-846 Method 9030B/9034	Not applicable – iodimetric titration	Not applicable	Not applicable
Ammonia by Method 350.1	Initial: Daily	3-point calibration plus mid-level and blank	r ≥ 0.997 ±10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±10% of true value Not > RL
	Ending	Mid-level plus blank	±10% of true value Not > RL

Table B-8 Analytical Instrument Calibration (Page 3 of 5)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Silica by Method 370.1	Initial: Daily	8-point calibration plus mid-level plus blank	r ≥ 0.997 ± 10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	± 10% of true value Not > RL
	Ending	Mid-level plus blank	± 10% of true value Not > RL
TSS by Method 160.2	Not applicable – weight method	Not applicable	Not applicable
Ortho-Phosphate by Method 365.1	Initial: Daily	8-point calibration plus mid-level plus blank	r ≥ 0.997 ± 10% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	± 10% of true value Not > RL
	Ending	Mid-level plus blank	± 10% of true value Not > RL
Surfactants (MBAS) by Method 425.1	Initial: Every 6 months, or as needed	10-point calibration	r ≥ 0.995
	Continuing: Every 10 samples	Mid-level calibration	80-120% true value
	Ending:	Mid-level calibration	80-120% true value
Grain Size Distribution by ASTM 422-63	NA	NA	NA
Bulk Density by ASTM D5057	NA	NA	NA
DOC by Method 415.1	Initial: As needed	4-point calibration plus blank	r ≥ 0.997 ±15% of true value Not > RL
	Continuing: Every 10 samples	Mid-level plus blank	±15% of true value Not > RL
	Ending	Mid-level plus blank	±15% of true value Not > RL

Table B-8 Analytical Instrument Calibration (Page 4 of 5)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
Ra-226 by Method 903.1	Initial: Efficiency calibration (annual or when daily check not within limits)	NIST Traceable Standards	Standard deviation < 10% of cell constant average
	Verification	NIST Traceable Standards	75-125%R
	Daily: Instrument Performance Check	NIST Traceable Source	Within 2-3 sigma of historical limits
	Background count for each Lucas cell to be used before every calibration and verification		Record count for each Lucas cell in a logbook, must be less than 0.267 cpm
Ra-228 by Method 904.0	Annual energy and efficiency calibration	NIST Traceable Standards	Minimum of 10,000 counts
	Daily efficiency calibration check	NIST Traceable Standards	Within 2-3 sigma control limits
	Weekly Background		Within 2-3 sigma control limits
Isotopic Uranium by Method HASL 300	Daily Pulser Check (peak centroid, pulser count rate, peak FWHM)	NIST Traceable standards	
	Monthly Efficiency Calibration (energy and efficiency)	NIST Traceable standards	Within 2-3 sigma control limits
	Weekly Background		Within 2-3 sigma control limits
Hardness by SM 2340B (calculation)	NA	NA	NA

Table B-8 Analytical Instrument Calibration (Page 5 of 5)

Instrument and Method	Calibration Frequency	Calibration Standards	Acceptance Criteria[1]
TOC by Lloyd Kahn Method	Initial: As needed	1 pt calibration checked by 6 concentrations covering range of analysis	±15% of true value Not > RL
	Continuing: Every 10 samples	1 pt calibration checked by 6 concentrations covering range of analysis	±15% of true value Not > RL
	Ending	1 pt calibration checked by 6 concentrations covering range of analysis	±15% of true value Not > RL
Boron Isotope Ratios by TIMS	Prior to Analysis	One standard goes through separation process	Standard has known ratio and is used to compare to sample (correction ratio)
		One standard not prepped	Standard has known ratio and is used to compare to sample (correction ratio)
Tritium by Enrichment and low-level proportional counting	Background: at least once weekly for each counter	Count dead hydrogen as (from petroleum)	Sets background count of the counting equipment
	Blank of NaOH: each batch	Tested for blank value	Sets blank value for NaOH batch
	Process blanks: once a week	Dead water (from Floridian aquifer)	Sets blank value of dead water
	Efficiency of Enrichment Process: at least once weekly	Sample of known activity processed through entire system of enrichment, reduction, and counting	Sets efficiency of each counter
Total Coliform/ Escherichia Coli	NA	NA	NA

[1]= If criteria are not met, corrective actions as specified in the laboratory SOPs (Attachment D), are taken.

NA = Not Applicable

ATTACHMENT A

HUMAN HEALTH AND ECOLOGICAL DATA QUALITY LEVELS

QAPP ATTACHMENT A

This appendix provides the human health and ecological risk-based data quality levels (DQLs) that were used by the laboratories to identify the methods appropriate for analysis of each environmental medium/constituent combination. Based on the work proposed in the Field Sampling Plan (FSP), DQLs are provided for inorganics in water (Table A-1), inorganics in sediment (Table A-2), radionuclides in water (Table A-3), and inorganics in solid matrices (Table A-4).

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Attachment A
Table A-1
Human Health and Ecological
Data Quality Levels (DQL) for Inorganics in Water
Pines Area of Investigation

		Human Health					Ecological					Final
		Tapwater PRG (a)		MCL (c)	RAL (d)	Selected Human Health DQL (e)	Federal AWQC (f)	Indiana WQC (g)	Region 5 ESL (h)	Secondary Chronic Value (i)	Selected Ecological DQL (j)	Selected Water DQL (k)
Constituent	CAS Number	(ug/L)	Basis	(ug/L)	(ug/L)	(ug/L)	(ugL)	(ugL)	(ug/L)	(ug/L)	(ug/L)	(ug/L)
Aluminum	7429-90-5	3.60E+04	NC	NA	NA	3.60E+04	8.70E+01	NA	NA	NA	8.70E+01	8.70E+01
Arsenic	7440-38-2	4.50E-02	C	1.00E+01	5.00E+01	4.50E-02	1.50E+02	NA	1.47E+02	3.10E+00	1.50E+02	4.50E-02
Barium	7440-39-3	2.60E+03	NC	2.00E+03	2.00E+03	2.00E+03	4.00E+00	NA	2.20E+02	4.00E+00	4.00E+00	4.00E+00
Boron	7440-42-8	7.30E+03	NC	NA	9.00E+02	9.00E+02	NA	NA	NA	1.60E+00	1.60E+00	1.60E+00
Cadmium	7440-43-9	1.80E+01	NC	5.00E+00	5.00E+00	5.00E+00	2.46E-01	2.20E+00	1.50E-01	NA	2.46E-01	2.46E-01
Calcium	7440-70-2	EN		EN	EN	EN	EN	EN	EN	EN	EN	EN
Chromium	7440-47-3	1.10E+02 (b)	NC	1.00E+02	2.00E+02	1.00E+02	1.10E+01	1.10E+01	4.20E+01	NA	1.10E+01	1.10E+01
Copper	7440-50-8	1.50E+03	NC	1.30E+03	1.30E+03	1.30E+03	8.96E+00	9.00E+00	1.58E+00	NA	8.96E+00	8.96E+00
Iron	7439-89-6	EN		EN	EN	EN	1.00E+03	NA	NA	NA	1.00E+03	1.00E+03
Lead	7439-92-1	NA		1.50E+01	3.00E+01	1.50E+01	2.52E+00	3.00E+00	1.17E+00	NA	2.52E+00	2.52E+00
Magnesium	7439-95-4	EN		EN	EN	EN	EN	EN	EN	EN	EN	EN
Manganese	7439-96-5	8.80E+02	NC	NA	NA	8.80E+02	1.20E+02	NA	NA	1.20E+02	1.20E+02	1.20E+02
Molybdenum	7439-97-7	1.80E+02	NC	NA	1.00E+01	1.00E+01	NA	NA	NA	3.70E+02	3.70E+02	1.00E+01
Nickel	7440-02-0	7.30E+02	NC	NA	5.00E+02	5.00E+02	5.20E+01	5.20E+01	NA	NA	5.20E+01	5.20E+01
Potassium	7440-09-7	EN		EN	EN	EN	EN	EN	EN	EN	EN	EN
Selenium	7782-49-2	1.80E+02	NC	5.00E+01	2.00E+02	5.00E+01	4.61E+00	5.00E+00	5.00E+00	NA	4.61E+00	4.61E+00
Sodium	7440-23-5	EN		EN	EN	EN	EN	EN	EN	EN	EN	EN
Strontium	7440-24-6	2.20E+04	NC	NA	2.50E+04	2.20E+04	NA	NA	NA	1.50E+03	1.50E+03	1.50E+03
Thallium	7440-28-0	2.40E+00	NC	2.00E+00	2.00E+00	2.00E+00	1.20E+01	NA	1.00E+01	1.20E+01	1.20E+01	2.00E+00
Vanadium	7440-62-2	3.60E+01	NC	NA	2.50E+02	3.60E+01	2.00E+01	NA	1.20E+01	2.00E+01	2.00E+01	2.00E+01
Zinc	7440-66-6	1.10E+04	NC	NA	3.00E+03	3.00E+03	1.18E+02	1.20E+02	6.57E+01	NA	1.18E+02	1.18E+02

Notes:
AWQC - Ambient Water Quality Criteria.
C - Potentially carcinogenic effects.
CAS - Chemical Abstracts Service.
DQL - Data Quality Level.
EN - Essential nutrient.
ESL - Ecological Screening Level.
MCL - Maximum Contaminant Level.
NA - Not Available.
NC - Noncarcinogenic effects.
PRG - Preliminary Remediation Goal.
RAL - Removal Action Level.
SCV - Secondary Chronic Value.
WQC - Water Quality Criteria.
(a) - USEPA. 2004a. USEPA Region 9 PRG Table. October 2004. Value for tapwater.
(b) - PRG for hexavalent chromium (no total chromium 1:6 ratio value available for tapwater).
(c) - USEPA. 2004b. Drinking Water Standards and Health Advisories. Winter 2004.
(d) - USEPA. 1998. Resubmittal of the Latest Superfund Removal Action Levels. Office of Solid Waste and Emergency Response. USEPA. November 10, 1998.
(e) - Lower of PRG/MCL/RAL.
(f) - Chronic freshwater AWQC obtained from USEPA National Recommended Water Quailiity Criteria: 2002. Dissolved criteria presented if applicable.
(g) - Indiana Administrative Code. Title 327, Article 2, Rule 1.5-8 Water Quality Standards Applicable to All State Waters Within the Great Lakes System. Minimum Surface Water Quality Criteria. Table 8-1 Water Quality Criteria for the Protection of Aquatic Life.
(h) - USEPA. 2003. USEPA Region 5 Ecological Screening Level for water. Updated August 22, 2003. (http://www.epa.gov/reg5rcra/ca/ESL.pdf)
(i) - Secondary chronic value obtained from *Toxicological Benchmarks for Screening Contaminants of Concern for Effects on Aquatic Biota* (Suter and Tsao, 1996).
(j) - Selected according to the following hierarchy: lower of the AWQC and Indiana WQC, then ESL, SCV.
(k) - Lower of human health and ecological DQLs.

Attachment A
Table A-2
Human Health and Ecological
Data Quality Levels (DQL) for Inorganics in Sediment
Pines Area of Investigation

		Human Health		Ecological			Final
Constituent	CAS Number	Residential Soil PRG (a) (mg/kg)	Basis	Region 5 ESL (d) (mg/kg)	Other Ecological Screening Values (mg/kg)	Selected Sediment DQL (g) (mg/kg)	Selected DQL (h) (mg/kg)
Aluminum	7429-90-5	7.60E+04	NC	NA	2.55E+04 (f)	2.55E+04	2.55E+04
Arsenic	7440-38-2	3.90E-01	C	9.79E+00	NA	9.79E+00	3.90E-01
Barium	7440-39-3	5.40E+03	NC	NA	NA	NA	5.40E+03
Boron	7440-42-8	1.60E+04	NC	NA	NA	NA	1.60E+04
Cadmium	7440-43-9	3.70E+01	NC	9.90E-01	NA	9.90E-01	9.90E-01
Calcium	7440-70-2	EN		EN	NA	EN	EN
Chromium (total)	7440-47-3	2.10E+02 (b)	C	4.34E+01	NA	4.34E+01	4.34E+01
Copper	7440-50-8	3.10E+03	NC	3.16E+01	NA	3.16E+01	3.16E+01
Iron	7439-89-6	EN		NA	2.00E+04 (e)	2.00E+04	2.00E+04
Lead	7439-92-1	4.00E+02	NC (c)	3.58E+01	NA	3.58E+01	3.58E+01
Magnesium	7439-95-4	EN		EN	NA	EN	EN
Manganese	7439-96-5	1.80E+03	NC	NA	4.60E+02 (e)	4.60E+02	4.60E+02
Molybdenum	7439-97-7	3.90E+02	NC	NA	NA	NA	3.90E+02
Nickel	7440-02-0	1.60E+03	NC	NA	1.60E+01 (e)	1.60E+01	1.60E+01
Potassium	7440-09-7	EN		EN	NA	EN	EN
Selenium	7782-49-2	3.90E+02	NC	NA	2.90E-01 (f)	2.90E-01	2.90E-01
Sodium	7440-23-5	EN		EN	NA	EN	EN
Thallium	7440-28-0	5.20E+00	NC	NA	NA	NA	5.20E+00
Vanadium	7440-62-2	7.80E+01	NC	NA	5.00E+01 (f)	5.00E+01	5.00E+01
Zinc	7440-66-6	2.30E+04	NC	1.21E+02	NA	1.21E+02	1.21E+02

Notes:
C - Potentially carcinogenic effects.
CAS - Chemical Abstracts Service.
DQL - Data Quality Level.
EN - Essential nutrient.
ER-L - Effects Range-Low.
ESL - Ecological Screening Level.
LEL - Lowest Effect Level.
NA - Not Available.
NC - Noncarcinogenic effects.
NOAA - National Oceanic and Atmospheric Administration.
PRG - Preliminary Remediation Goal.
(a) - USEPA. 2004a. USEPA Region 9 PRG Table. October 2004. Value for residential soil.
(b) - PRG for total chromium (1:6 ratio hexavalent:trivalent).
(c) - PRG for lead is based on noncarcinogenic effects, developed using and integrated exposure model (USEPA, 1996).
(d) - USEPA. 2003. USEPA Region 5 Ecological Screening Level for sediment. Updated August 22, 2003. (http://www.epa.gov/reg5rcra/ca/ESL.pdf)
(e) - LELs from Ontario Ministry of the Environment (Persaud, et al, 1996).
(f) - Value from NOAA's Screening Quick Reference Table (Buchman, 1999).
(g) - Selected according to the following hierarchy: ESL, LEL, ER-L, Screening Quick Reference Table value.
(h) - Lower of PRG/selected ecological DQL.

Attachment A
Table A-3
Human Health Data Quality Levels (DQL) for Radionuclides in Water
Pines Area of Investigation

Isotope	Element (Atomic Number)	Tapwater PRG (a) (pCi/L)
Ra-226	Radium (88)	0.00082
Ra-228	Radium (88)	0.0458
U-234	Uranium (92)	0.674
U-235	Uranium (92)	0.684
U-238	Uranium (92)	0.744

Notes:
(a) - Radionuclide Toxicity and Preliminary Remediation Goals (PRGs) for Superfund. August 4, 2004. (http://epa-prgs.ornl.gov/radionuclides/).

Attachment A
Table A-4
Human Health and Ecological
Data Quality Levels (DQL) for Inorganics in Coal-Combustion By-Products (CCBs)
Pines Area of Investigation

Analyte	CAS Number	Human Health: Residential Soil PRG (a) (mg/kg)		Human Health: Basis	Ecological: Eco SSL (f) (mg/kg)	Ecological: Region 5 ESL (g) (mg/kg)	Ecological: ORNL Phytotoxicity Screening Values (h) (mg/kg)	Ecological: Selected Ecological DQL (i) (mg/kg)	Final Selected DQL (j) (mg/kg)
Aluminum	7429-90-5	76000		NC	NA	NA	50	50	50
Antimony	7440-36-0	31		NC	0.29	NA	NA	0.29	0.29
Arsenic	7440-38-2	0.39		C	NA	5.7	NA	5.7	0.39
Barium	7440-39-3	5400		NC	330	NA	NA	330	330.0
Beryllium	7440-41-7	150		NC	36	NA	NA	36	36.0
Boron	7440-42-8	16000		NC	NA	NA	0.5	0.5	0.50
Cadmium	7440-43-9	37		NC	0.38	NA	NA	0.38	0.3800
Calcium	7440-70-2	EN			EN	EN	EN	EN	EN
Chromium (total)	7440-47-3	210	(b)	C	NA	0.4	NA	0.4	0.40
Cobalt	7440-48-4	900		NC	13	NA	NA	13	13.00
Copper	7440-50-8	3100		NC	NA	5.4	NA	5.4	5.4
Iron	7439-89-6	EN			NA	NA	NA	NA	0
Lead	7439-92-1	400		NC (d)	16	NA	NA	16	16
Magnesium	7439-95-4	EN			EN	EN	EN	EN	EN
Manganese	7439-96-5	1800		NC	NA	NA	500	500	500
Mercury	7439-97-6	23	(c)	NC	NA	0.1	NA	0.1	0.1
Molybdenum	7439-97-7	390		NC	NA	NA	2	2	2
Nickel	7440-02-0	1600		NC	NA	NA	30	30	30
Potassium	7440-09-7	EN			EN	EN	EN	EN	EN
Selenium	7782-49-2	390		NC	NA	0.0276	NA	0.028	0.028
Silicon	7631-86-9	No PRG		(e)	NA	NA	NA	NA	(f)
Silver	7440-22-4	390		NC	NA	4.04	NA	4.0	4.0
Sodium	7440-23-5	EN			EN	EN	EN	EN	EN
Thallium	7440-28-0	5.2		NC	NA	0.0569	NA	0.0569	0.057
Vanadium	7440-62-2	78		NC	NA	1.59	NA	1.6	1.6
Zinc	7440-66-6	23000		NC	NA	6.62	NA	6.6	6.6

Notes:
C - Potentially carcinogenic effects.
CAS - Chemical Abstracts Service.
EN - Essential nutrient. No PRG available.
ESL - Ecological Screening Level.
NC - Noncarcinogenic effects.
PRG - Preliminary Remediation Goal.
ORNL - Oak Ridge National Laboratory.
SSL - Soil Screening Value.
(a) - U.S. EPA Region 9 PRG Table. October 2004. Value for residential soil.
(b) - PRG for total chromium (1:6 ratio hexavalent:trivalent)
(c) - PRG for mercury and compounds.
(d) - PRG for lead is based on noncarcinogenic effects, but was developed using and integrated exposure model.
(e) - Included on constituent list for evaluation of general chemistry and fate and transport.
Laboratory to determine achievable detection limits.
(f) - EcoSSLs obtained from http://www.epa.gov/ecotox/ecossl/. Value presented is lowest available for plant, soil invertebrate, bird, and mammal.
(g) - U.S. EPA Region 5 Ecological Screening Level for soil. Updated August 22, 2003. (http://www.epa.gov/reg5rcra/ca/ESL.pdf)
(h) - ORNL screening benchmark for terrestrial plants (Efroymson, et al., 1997); values for earthworms are higher.
(i) - Selected according to the following hierarchy: Eco-SSL, ESL, ORNL phytotoxicity screening value.
(k) - Lower of PRG/selected ecological DQL.

ATTACHMENT B

FIELD STANDARD OPERATING PROCEDURES

Field Change Order Procedures

SOP Number 100Pines

Revision Number: 2.0

January 2005

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January 18, 2005

Debra L. McGrath

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January 18, 2005

ENSR Corporation
January 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FCO	Field Change Order
FSP	Field Sampling Plan
HASP	Health and Safety Plan
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RI	Remedial Investigation
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes field change order (FCO) procedures applicable to ENSR sampling and analysis programs.

2.0 SUMMARY OF METHOD

Procedural changes in the field can be needed when the sample network is changed (i.e., fewer or more samples, adjustments to locations) or when field procedures require modification due to unexpected conditions. Changes made in the field will be documented on an FCO form (see Figure 1).

3.0 HEALTH AND SAFETY WARNINGS

Not applicable.

4.0 INTERFERENCES

Not applicable.

5.0 PERSONNEL QUALIFICATIONS

Individuals responsible for completing FCO documentation must be personnel working on the specific field program for which the change is necessary, have read this SOP, and have worked under the oversight of experienced personnel.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- FCO Form (Figure 1)
- Field project logbook/pen
- Approved plans (e.g., FSP, QAPP, HASP)

7.0 METHODS

7.1 Field Change Order

7.1.1 The field personnel and/or the Field Operations Leader will recommend a change in consultation with the ENSR Project Manager, the ENSR Remedial Investigation (RI) Task Manager, and/or the ENSR Project Quality Assurance (QA) Officer. The ENSR Project Manager, RI Task Manager, or QA Officer will approve the change, which will be implemented by the field personnel. Approval may initially be received verbally or electronically, but will be documented on the FCO, as detailed below.

7.1.2 The following information shall be completed on the FCO form (Figure 1):

- Date
- Project name
- Project number
- Description of change and reason and justification for change, including reference to section(s) of Work Plan(s) affected
- Field personnel or Field Operations Leader signature and date
- Project Manager, RI Task Manager, or QA Officer signature and date

7.1.3 Field changes will be implemented and documented in the field logbook. No field personnel will initiate field changes without prior communication of findings through the proper channels. Thus, communication will be documented in the field logbook and FCO form.

8.0 DATA AND RECORDS MANAGEMENT

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Quality control will consist of implementing the field change process as described above, including the appropriate approval process.

10.0 REFERENCES

Not applicable.

FIGURE 1 - Example Field Change Order Form

Field Change Order (FCO)

DATE:
PROJECT NAME: Pines RI/FS
PROJECT NUMBER: 01776-020

DESCRIPTION OF CHANGE AND RATIONALE

SIGNATURE APPROVALS

IN THE FIELD: ______________________________ DATE: ______________

MANAGEMENT: ______________________________ DATE: ______________

Management may include RI Task Manager, Project Manager and/or QA Officer.

ENSR INTERNATIONAL

Water Level Measurements

SOP Number 101Pines

Revision Number: 2.0

May 2005

ENSR Project Manager
May 23, 2005

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
QAPP	Quality Assurance Project Plan
OSHA	Occupational Safety and Health Administration
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operation Procedure (SOP) describes the methods to be used for measuring depth to groundwater levels and total depth of groundwater monitoring wells and piezometers. Similar procedures will also be used to measure the depth to water in surface water bodies from fixed structures such as bridges or culverts.

Water level and well depth measurements collected from monitoring wells or piezometers are used to assess:

- The horizontal hydraulic gradient and the direction of groundwater flow;
- The vertical hydraulic gradient, if well nests are used (i.e., the direction of groundwater flow in the vertical plane); and
- The calibration of a numerical groundwater flow model.

This information, when combined with other location-specific information, such as hydraulic conductivity or transmissivity, may be used to estimate the rate of constituent movement, etc. Total well depth measurements are also collected as an indicator of siltation within the well column, and to calculate well volumes if necessary.

2.0 SUMMARY OF METHOD

Measurements will involve measuring the depth to water or total well depth to the nearest 0.01 foot using an electronic probe (water level meter). The depths within wells will be measured from the top of the inner casing at the surveyed elevation point as marked on the top of the inner casing. Depths to surface water will be measured from a mark placed on the fixed structure (e.g., bridge, culvert) by the surveyor.

3.0 HEALTH AND SAFETY WARNINGS

Collecting water level measurements may involve chemical hazards associated with materials in the water being in contact with the water level measurement equipment. When collecting water level measurements, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result in inaccurate readings if the sensor on the water level meter is wet or dirty, or if the cable cannot be kept vertically upright (for example, from a bridge in the wind). Care shall be taken to keep the probe clean. If wells are not installed plumb, the probe may rest against the side of the well, which may be wet. Care shall be taken in measuring water levels to reduce these interferences. If there is any concern that a particular reading may not be accurate, this shall be noted in the field log book.

5.0 PERSONNEL QUALIFICATIONS

Collecting water level measurements is a relatively simple procedure requiring minimal training and a relatively small amount of equipment. It is recommended that the collection of water level measurements be initially supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP and health and safety requirements outlined within the Field Sampling Plan (FSP) and HASP. Field personnel are responsible for the proper use, maintenance, and decontamination of all equipment used for obtaining water level measurements, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT AND SUPPLIES

6.1 Electronic Water Level Meter

Electronic water level meters consist of a spool of small-diameter cable (or tape) with a weighted probe attached to the end. The cable (or tape) is marked with measurement increments in feet (accurate to 0.01 feet), with the zero point being the tip of the probe. When the probe comes in contact with the water, an electrical circuit is closed, and a light and/or buzzer within the spool will signal the contact. The probe shall be tested at the start of the field program to ensure proper operation.

6.2 Other Materials

Other materials that may be required:

- Health and safety supplies (as required by the HASP)
- Equipment decontamination materials (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Plastic sheeting or bucket for resting instrument off the ground
- Water level field form (if applicable)
- Well construction records
- Approved plans (e.g., FSP, QAPP, HASP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

7.1.1 Well Records Review: Well completion diagrams should be reviewed to determine well construction characteristics. Historic static water level measurements and survey information should also be reviewed.

7.1.2 Water Level/Well Depth Measurement: The water level and well depth should be measured with a water level meter and written in the field logbook or field form. This information is used to calculate groundwater elevations. All data will be maintained in the project files.

7.1.3 Equipment Decontamination: All equipment should be decontaminated prior to use and between well locations in accordance with ENSR SOP No. 7600Pines - Decontamination of Field Equipment.

7.2 Measurement Procedures

7.2.1 At each location (well, piezometer, staff gauge, etc.), determine the location of the surveyed elevation mark. For wells, general markings include either a notch in the riser pipe or a permanent ink (generally black ink) mark on the riser pipe. For monitoring surface water levels, there may be a painted mark on an existing structure or the reference point must be known if not painted.

7.2.2 To obtain a water level measurement, lower the probe of a water level meter down into the water until the audible sound of the unit is detected or the light on an electronic sounder illuminates. In wells, the probe shall be lowered slowly into the well to avoid disruption of formation water and creation of turbulent surface water within the well. At this time, the precise measurement should be determined (to nearest 0.01 feet) by repeatedly raising and lowering the tape to converge on the exact measurement. Obtain the reading from the surveyed elevation mark.

7.2.3 Record the water level measurement as well as the location identification number, measuring point (surveyed elevation point), date, time, and weather conditions in the field logbook and/or field form.

7.2.4 To measure the total depth of a well, lower the probe (turn down signal as appropriate) slowly to the bottom of the well. The depth may be difficult to determine for wells with “soft” or silty bottoms. It may be helpful to lower the probe until there is slack in the tape, and gently pull up until it feels as if there is a weight at the end of the tape. Observe the measurement (to the nearest 0.01 foot) of the tape against the surveyed elevation mark.

7.2.5 Record the total well depth in the field logbook and/or field form.

7.2.6 The meter will be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Generally, only that portion of the tape that enters the water table needs to be decontaminated. It is important that the measuring tape is never placed directly on the ground surface or allowed to become kinked.

8.0 DATA AND RECORDS MANAGEMENT

All field information will be recorded in the field logbook or on a field collection form by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the measurement process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel will follow specific quality assurance guidelines as outlined in the Quality Assurance Project Plan (QAPP) and/or FSP. Where measured depths are not consistent with well records or previously measurements, the depths should be re-measured and verified.

10.0 REFERENCES

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

ENSR INTERNATIONAL

In-Situ Hydraulic Conductivity Testing – Rising and Falling Head Permeability Tests

SOP Number 102Pines

Revision Number: 2.0

May 2005

Lisa M. Bradley

ENSR Project Manager
May 23, 2005

Debra L. McGrath

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Administration
SOP	Standard Operating Procedure
QAPP	Quality Assurance Project Plan

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures for conducting in-situ rising head and falling head hydraulic conductivity tests (slug tests). Slug tests are performed to assess the hydraulic conductivity of the soil or rock surrounding the tested monitoring well.

Hydraulic conductivity values are used:

- To estimate rates of groundwater flow;
- To estimate responses of aquifers to applied stresses, such as pumping;
- To estimate the rate of movement of various chemicals in subsurface zones; and
- To construct and calibrate groundwater flow models.

In-situ tests to determine hydraulic conductivity can be conducted in open boreholes or in monitoring wells and they can be variable-head tests or constant-head tests. The change in water levels can be produced by displacing a known volume of water using a slug. The response of water levels to the test can be monitored using a water level tape or with computerized data loggers. Data loggers are preferred because they can collect many measurements in a short period of time, which is important for evaluating the early-time response of the aquifer to the slug. For the purpose of this SOP and the field program outlined in the Field Sampling Plan (FSP), the method to perform a variable-head test in a monitoring well using a computerized data logger will be outlined.

2.0 SUMMARY OF METHOD

Hydraulic conductivity is a measure of the ease of flow of water through a specific porous medium. Variable-head tests are performed by causing a sudden (instantaneous) rise or drop of the static water level in a well. Water levels are monitored and recorded until the water level has returned to static conditions or sufficient data is collected to perform the hydraulic conductivity calculations.

3.0 HEALTH AND SAFETY WARNINGS

Hydraulic conductivity testing may involve chemical hazards associated with exposure to groundwater and the testing equipment that comes in contact with the groundwater. When conducting hydraulic conductivity tests, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

There are many potential interferences in the performance and analysis of slug tests. For this reason, appropriately trained personnel shall perform the tests in the field and conduct the data analysis. Data and analysis will be reviewed by a geologist licensed to practice in Indiana.

One of the primary interferences is due to well construction. For wells screened across the water table, falling head tests may not provide accurate measures of hydraulic conductivity. Therefore, while falling head tests may be conducted in such wells, their results will not be used quantitatively unless the data analysis indicates that an accurate measurement of hydraulic conductivity has been obtained.

5.0 PERSONNEL QUALIFICATIONS

Field personnel conducting permeability tests should be experienced geologists familiar with the theory and practice of aquifer testing and analysis, as well as with all necessary equipment and software. Geologists or personnel with geologic experience should supervise hydraulic conductivity testing. The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field personnel to be familiar with the hydraulic conductivity testing procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within the FSP, the Quality Assurance Project Plan (QAPP), and the HASP. Field personnel are responsible for the proper testing procedures, decontamination of equipment, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Boring logs (if available)
- Well construction diagrams (if available)
- Well development logs (if available)
- Hydraulic Conductivity Test Log (Figure 1)
- Water level meter
- Slugs
- Nylon string
- Tape measure
- Pressure transducer(s)
- Data logger(s)
- Computer with appropriate software
- Plastic sheeting
- Equipment decontamination materials (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

The monitoring wells to be tested should have been previously developed and had sufficient time to equilibrate before the testing process proceeds. Well construction diagrams are necessary to determine the depth of the monitoring well and the screened interval.

The static water level in the well will be measured and recorded in the field logbook or field form. The slug diameter and length to be used in the well will be determined based on the diameter of the well and the length of the water column. In general, the larger the volume of the slug, the greater the displacement of head and the better the definition of response in the resulting data. However, the slug must be short enough to be completely submerged beneath the static water level, and there must be room beneath the bottom of the slug for the transducer. Therefore, a minimum of 7 feet of water within the well is typically necessary for conducting the test. The slug length and diameter will be recorded in the field logbook or field form for use in the data analysis.

Either a pressure transducer connected to a data logger or a programmable down-hole data logger will be used to record the changes in water level during the test. The transducer must be set at least one slug length below the water surface so the slug does not disturb the transducer. Several feet deeper is preferable, if possible. After the water level has equilibrated to the static level, the data logger will be programmed according to manufacture's instructions. The data logger will be programmed to record water levels at logarithmically increasing intervals, because early-response data is important for the data analysis.

A measured length of nylon string will be tied to the slug. The line will be of a length that will allow the top of the slug to be submerged beneath the static water level without touching the transducer.

7.2 Falling Head Test

The slug will be lowered part way into the well so that the bottom of the slug is just above the water surface. The data logger will be started and the slug will be simultaneously lowered into the water, so that the top of the slug is below the static water level. Care will be taken to lower the slug fast enough to produce as close to an instantaneous rise in the water level as possible, but not so fast as to produce a wave when the slug enters the water.

When the water level returns to the static level, the falling head test is complete and the rising head test can be started. The data should be saved and a new test set up on the data logger.

If the hydraulic conductivity is low, it may take hours (or more) for the water level to return to static conditions. In this situation, the project hydrogeologist should determine a maximum duration for each test (typically 30 minutes).

The falling head test may not be accurate for wells with screens that bracket the stabilized water table. These tests may be performed in water table wells, but the results will not be used quantitatively unless the data analysis indicates that an accurate measurement of hydraulic conductivity has been obtained.

7.3 Rising Head Test

After the data logger is reset following the falling head test, the test will be started by activating the logger and simultaneously removing the slug. The slug will be quickly removed from the water so that an instantaneous drop in the water level will occur, but it will be done smoothly enough to not disturb the transducer when removing the slug. When the water has returned to a static condition or the maximum duration of time has elapsed (typically 30 minutes), the test will be terminated.

7.4 Data Download

At the completion of the test(s), the data from the slug tests will be downloaded to a laptop computer. If feasible, this data will be plotted on a graph of time versus water level to see if it is acceptable (i.e., adequate water level displacement, sufficient number of data points, a straight-line fit to data, no extraneous fluctuations resulting from inadvertent slug movement and/or pressure waves). If the data are not acceptable, the test(s) will be repeated once water levels have stabilized.

7.5 Equipment Decontamination

All equipment that comes into contact with groundwater (e.g., slugs, transducer, and water level meter) will be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment before moving to the next location. The string should be properly discarded and disposed of.

8.0 DATA AND RECORDS MANAGEMENT

8.1 Data Analysis

Several methods are available for analyzing data obtained from in-situ hydraulic conductivity tests. Most methods incorporate graphical techniques, such as semi-log and log-log plots, to evaluate the data and select values for the calculations.

Inherent in the analytical methods are several simplifying assumptions concerning the aquifer properties and test methods. When selecting a particular analytical method, it is important to consider the basic assumptions that underlie the mathematical expressions. In many cases, it may be advisable to evaluate the data using several methods and examine the range of hydraulic conductivity values that are obtained. For this project, it is expected that the data will be analyzed using appropriate methodologies (e.g., Bouwer and Rice, 1976; Kansas Geological Survey methods (Hyder, et al., 1994); Cooper, et al, 1967).

8.2 Records Management

The Hydraulic Conductivity Test Log (Figure 1) will be completed by the field personnel conducting the slug testing. Background information such as well diameter, depth, and screened interval will be provided from existing monitoring well construction logs. These data will be used in the calculation of hydraulic conductivity, based on the test data. The slug length, slug diameter, water level, well identification number, test type (rising or falling), file name, and time will also be recorded. The actual data of time versus water level will be recorded on the data logger and transferred to a laptop computer. In addition, a field project notebook should be maintained detailing any problems or unusual conditions that may have occurred during the testing process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Quality assurance requirements typically suggest the collection of both the rising head and falling head data. Rising head data are preferred for wells screened across the water table because the hydraulic conductivity of the saturated portion of the aquifer is reflected, whereas falling head data may reflect the hydraulic conductivity of the unsaturated zone and capillary fringe.

For quality control purposes, the transducer data logging will be started immediately prior to lowering or removing the slug. The transducer should be activated approximately 1 second prior to ensure that the transducer is recording water level changes and that the transducer is taking readings at frequent intervals during the early part of the well response curve. Care must be taken when lowering or removing the slug to avoid splashing or generating wave effects that would obscure the early-time data.

Data from the rising and falling head tests should be inspected in graphical format to ensure that adequate water level displacement was achieved for both tests, that the data logger recorded all data from the test, and that no fluctuations exist in the data due to violent slug movement.

Both rising and falling head tests may be conducted to help draw attention to any inconsistencies in the data. If the rising and falling head results are not comparable, the data should be investigated to assess which test may more accurately reflect the hydraulic properties of the aquifer, or whether the pressure transducer recorded accurate data. Knowledge of the boring logs is essential to assessing whether the measured response is consistent with the expected response. If a consistent response is not obtained, the tests should be run again.

The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana. Data and analysis will be reviewed by the licensed Indiana geologist.

10.0 REFERENCES

Bouwer, H and RC Rice. 1976. A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. Water Resources Research, Vol. 12, pp. 423-428.

Cooper, H Jr., D Bredehoeft, and S Papadopulos. 1967. Response of a Finite-Diameter Well to an Instantaneous Charge of Water. Water Resources Research, Vol. 3, No. 1.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

Hyder, Z, JJ Butler, Jr, CD McElwee, and W Liu. 1994. Slug tests in partially penetrating wells. Water Resources Research, Vol. 30, No. 11: 2945-2957.

FIGURE 1 – EXAMPLE HYDRAULIC CONDUCTIVITY TEST LOG (PAGE 1)

Well ID:

HYDRAULIC CONDUCTIVITY TEST LOG

Client: ________ Date: ________ Time: Start ______ am/pm
Project No: ________ Finish ______ am/pm
Site Location: ________
Weather Conds: ________ Tester (s): ________

1. WELL INFORMATION

a. Ref. Point Elev. ______ e. Total Well Depth ______ i. Screen Length ______

b. Static Depth to GW ______ f. Gravel Pack Diameter ______ j. Geology of Screened Interval

c. Time of GW reading ______ g. Water Column Height ______ (e-b) ________

d. Static GW Elev.(Ho) ______ (a-b) h. Casing Diameter ______ ________

2. SLUG INFORMATION (see back for volume calculation)

a. Slug Length ______

b. Slug Diameter ______

3. DATA COLLECTION

a. Method of Data Collection: Manual ______ (see back) Electronic ______

b. Transducer Information
- Make ______
- Model ______
- Serial Number ______
- Offset ______
- Linearity ______
- Scale ______
- Coefficient ______
- Diameter/Length ______

c. Data Logging Information
- Make ______
- Model ______
- Serial Number ______
- Mode ______ (linear or logarithmic)
- Ref. Point (designation) ______ (TOC, Ground Surface, actual elev.)
- Ref. Point value (if elev.) ______
- Positive numbers indicate increase or decrease in water level (circle one)

4. HYDRAULIC TEST INFORMATION

Start Time	Test Type (rising, falling)	Electronic File Name	Comments	End Time

5. MANUAL WATER LEVEL READINGS (as needed for control)

Time	Location	Depth to Water	Time	Location	Depth to Water

Signature ________ Date ________

FIGURE 1 – EXAMPLE HYDRAULIC CONDUCTIVITY TEST LOG (PAGE 2)

6. EXPECTED WATER LEVEL DISPLACEMENT CALCULATION (optional)

a. Diameter of Slug (in) ________
b. Length of Slug (ft) ________
c. Volume/Linear ft of Slug (gal/ft from chart) ________
d. Volume of Slug (gal) ________ (b*c)
e. Diameter of Well (in) ________
f. Volume/Linear ft of Well (gal/ft from chart) ________
g. Expected Change in Water Level ________ (d/f)

Volume / Linear Ft. of Pipe		
Diam. (in)	Gallon	Liter
0.25	0.0025	0.0097
0.375	0.0057	0.0217
0.5	0.0102	0.0386
0.75	0.0229	0.0869
1	0.0408	0.1544
1.25	0.0637	0.2413
1.5	0.0918	0.3475
2	0.1632	0.6178

Note: Water column height (1-g from front page) must be greater than transducer length plus length of slug.

7. MANUAL WATER LEVEL MEASUREMENTS

Time (HH:MM)	Elapsed Time (min)	Depth to Water from TOC (ft)	Head, h (TOC - water depth)	h/Ho	Comments
	0			1	

ENSR INTERNATIONAL

Surface Water and Sediment Sample Collection

SOP Number 103Pines

Revision Number: 3.0

September 2005

ENSR Project Manager
September 16, 2005

ENSR Project QA Officer
September 16, 2005

ENSR Corporation
September 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

DO	Dissolved Oxygen
FSP	Field Sampling Plan
HASP	Health and Safety Plan
MS/MSD	Matrix Spike/Matrix Spike Duplicate
ORP	Oxygen Reduction Potential
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the basic techniques and general considerations to be followed for the collection of surface water and sediment quality samples from streams and ponds. The specific details of actual sample collection are highly dependent upon local conditions as well as the purpose of the sampling.

2.0 SUMMARY OF METHOD

Surface water sample collection generally involves collection of a representative water sample from a water body (e.g., stream or pond) into an appropriate container. Specific field conditions such as water depth and location are recorded. Field parameters (e.g., pH, specific conductivity) are typically monitored as well.

Sediment sample collection generally involves collection of sediment via an apparatus (e.g., spatula, sediment corer, dredge, etc.) at the desired location and depth. The contents from the apparatus used to retrieve the sediment sample are typically de-watered to minimize the amount of water in the sample. The sample is then transferred to appropriate bottleware. Specific field conditions such as sediment description and depth and surface water depth are recorded.

3.0 HEALTH AND SAFETY WARNINGS

Surface water and sediment sampling may involve physical and/or chemical hazards associated with exposure to water, sediment, or materials in contact with either water or sediment. When surface water and sediment sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between sample locations or entrainment of non-target material in the samples. Minimization of the cross-contamination will occur through the following:

- Collection of samples from downstream to upstream locations.
- Collection of surface water samples prior to sediment samples at individual locations.
- The use of clean, decontaminated sampling tools at each location.
- Avoidance of material (e.g., re-suspended solids) that is not representative of the medium to be sampled.

5.0 PERSONNEL QUALIFICATIONS

Surface water and sediment sample collection is a relatively involved procedure requiring formal training and a variety of equipment. It is recommended that initial sampling be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field personnel to be familiar with the sampling procedures outlined within this SOP, with specific sampling, quality assurance, and health and safety requirements outlined within the Field Sampling Plan (FSP), Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for collecting samples, decontamination of equipment, and proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Surface Water and Sediment Sample Collection Record (Figure 1)
- Supplies for field filtration, if necessary (as required by ENSR SOP NO. 7131Pines – Field Filtration of Water Samples for Inorganic Constituents)
- Sample Chain-of-Custody forms (as required by ENSR SOP No. 1007Pines – Chain-of-Custody Procedures)
- Sample packaging and shipping supplies (as required by ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples)
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)

- Waterproof marker pens
- Individual or multi-parameter meter(s) to measure temperature, pH, specific conductance, dissolved oxygen (DO) oxidation reduction potential (ORP), and/or turbidity
- Instrument calibration solutions
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field notebook/pen

7.0 METHODS

7.1 Access to Sample Locations

Sample locations are presented in the FSP. Where samples are located at bridges or piers, these structures provide convenient access to for sampling. A boat may be needed to sample locations on ponds, as well as those on larger rivers. Frequently, however, a boat will take longer to cross a water body and will hinder manipulation of the sampling equipment. When boats are used for sampling, health and safety procedures as described in the HASP must be followed. Wading for samples will be used where water levels are appropriate (i.e., shallow) and there are no bridges or culverts nearby. If it is necessary to wade into the water body to obtain a sample, the sampler shall be careful to minimize disturbance of bottom sediments and must enter the water body downstream of the sampling location. If necessary, the sampling technician shall wait for the sediments to settle before taking a surface water sample.

Under ideal and uniform constituent dispersion conditions in a flowing stream, the same concentration of each constituent would occur at all points along the cross section. This situation is most likely downstream of areas of high turbulence. Careful selection of the sample collection location is needed in order to ensure, as nearly as possible, that samples are taken where uniform flow or dispersion and good mixing conditions exist.

7.2 Surface Water Sampling

7.2.1 General Procedures

Surface water samples from streams and ponds will be collected by filling a container at the desired depth. The sealed sample container is placed beneath the water surface at the desired depth. The sample container lid is then removed and allowed to fill with water. Once filled, the lid is then placed back on the container and then brought above the water surface.

In cases where sample bottles contain preservatives and the sample cannot be taken without potential loss or dilution of the preservative (e.g., shallow or low-flow conditions), a separate clean container (without preservatives) will be used for sampling and the contents carefully decanted into the final sample jar (with preservatives). The transfer container will be made of the same material as the final sample jar; in particular, no containers of glass will be used on this project due to potential interferences, unless they are guaranteed boron and silicon free. The transfer bottle may be submitted to the laboratory for other (unpreserved) analytes or disposed of after each sample. It will not be re-used at other sample locations.

Unless otherwise specified in the FSP, samples from streams should be collected at mid-depth in the mid-stream section or deepest flow channel of the stream that can be safely accessed. If a mid-stream position cannot be reached due to depth or other unsafe conditions, a water sample will be taken as close to mid-stream as can be safely reached from shore or shallower depths.

Water in ponds may be incompletely mixed especially if thermal stratification is present. Single samples can only represent the specific spot from which they were obtained. Therefore, more than one sample may be collected from different depths at each sample location within a pond, depending on the presence of thermal stratification.

Samples will be collected farthest downstream first, moving upstream so as to minimize the potential influence on water quality caused by disturbance within the water body.

At each sample location, measurements for pH, specific conductivity, temperature, DO, ORP, and/or turbidity will be collected using either an individual or a multi-parameter meter (e.g., ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor; ENSR SOP No. 108Pines – Field Measurement of Turbidity). The depth of water, depth of sample collection, and visual observations of the location will be recorded on the Surface Water and Sediment Collection Form (Figure 1) and/or field logbook. A qualitative estimate of stream flow rate will also be recorded when sampling surface water.

A portion of the water sample may be filtered in the field prior to preservation for analysis in the laboratory of dissolved fractions (e.g., selected metals). Filtration of water samples will follow the procedures outlined in ENSR SOP No. 7131Pines – Field Filtration of Water Samples for Inorganic Constituents.

7.2.2 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.
- Cap and label the container with (at a minimum) the sample identifier and sampling date and time. Additional information such as preservation information and analytical tests may also be added to the sample label as appropriate. Sample labeling will be conducted per the FSP and QAPP.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.
- Package the samples for shipment to the laboratory per ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

7.2.3 Equipment Decontamination

No equipment is necessary other than the sampling bottleware for sample collection. Therefore, no decontamination is necessary for surface water sampling.

7.3 Sediment Sampling

7.3.1 General Procedures

Sediment sampling may be accomplished by a variety of methods. Typical sediment sampling apparatus in shallow freshwater waterbodies includes sampling spatulas, sediment corers, and dredges, with the particular selection of apparatus dictated by the volume, depth, and nature of the sediments to be sampled.

The primary sediment sampling device will be a Russian peat borer (USEPA, 1999) that is designed to collect relatively uncompressed sediment samples. The components of the borer include a stainless steel, chambered core tube; extension rods; a stainless steel turning handle; and a core head and bottom point that support a stainless steel cover plate. The cover plate is curved and sharpened to minimize disturbance when the sampler is driven into the sediment. Once driven to the target depth, the core tube is rotated clockwise to fill the tube by cutting out a segment of sediment (USEPA, 1999). It can be used in both wadeable streams or in deeper waterbodies (using extensions) up to 10 feet deep in water depth.

The peat borer will be used to collect sediment samples from the stream bottom where sediments are 3 inches or greater. At shallower sediment depths (<3 inches), other means (e.g., stainless steel spatula) will be used to collect sediments.

Sediment samples are preferably located in areas of sediment depositional areas (e.g., pools, sand bars, debris dams) where finer-grained materials are more likely to settle out. Alternatively, deeper sections of ponds are areas where finer grained material would be expected to accumulate. A sketch or photograph of the sediment sampling location may be made to document its location relative to the stream channel or pond shoreline.

The method of sample collection in shallow, wadeable water bodies is accomplished by reaching over or wading into the water body and, while facing upstream (into a current, if it exists), using the sampling apparatus to obtain a sample from the upper 0 to 12 inches from the sediment horizon. Care should be taken to disturb the stratigraphy of the sediments as little as possible when sampling.

In deeper waters, lakes, reservoirs or impoundments, sampling will be conducted from a boat or overhanging structure (e.g., bridge). Sampling apparatus (e.g., corer, dredge) will be carefully lowered over the side of boat or structure until it reaches the bottom and the sample is obtained. Care should be taken during retrieval of the sample apparatus to prevent loss or disturbance of the sediments in the sampler during vertical transit upwards. Overlying water depth should be noted for deep water samples.

Samples will be collected farthest downstream first, moving upstream so as to minimize disturbance from within the water body. In cases, where no current is obvious (e.g., pond), samples may be taken systematically, provided sufficient distance is afforded to prevent re-suspended materials from early sampling efforts from influencing subsequent samples.

7.3.2 Sediment De-watering

Sediments with a high silt, clay or organic content or a flocculent appearance should be de-watered. Present U.S. Environmental Protection Agency (USEPA) analytical methods for sediment analysis are based on soil samples with percent moistures of less than 10%; whereas typically, sediments average 80% moisture. The increased percent moisture in sediments requires a larger wet weight sample size to obtain valid dry weight adjusted data. To address this issue, USEPA Region 1 recommends decanting all standing water from a sample prior to sample homogenization (USEPA, 1998). Decanting standing water should not include decanting of dispersed fine sediments. The sample may be further de-watered by lining a decontaminated stainless steel colander with Whatman #4 paper (or equivalent) and spreading the sediment in a thin layer on the filter paper for five to ten minutes. Additional sheets of filter paper may be necessary to sufficiently de-water the sample.

The de-watered sediment samples will then be placed into a decontaminated plastic mixing bowl. Each sample will be examined for physical characteristics such as composition, layering, odor, and discoloration. Descriptions will be recorded on the Surface Water and Sediment Sample Collection Record (Figure 1) and/or in the field logbook.

Following the examination of the sample for these physical features, the sample will be homogenized in the mixing bowl and placed into appropriate sample containers.

7.3.3 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.

- Cap and label the container with (at a minimum) the sample identifier and sampling date and time. Additional information such as preservation information and analytical tests may also be added to the sample label as appropriate. Sample labeling will be conducted per the FSP and QAPP.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.
- Package the samples for shipment to the laboratory per ENSR SOP No. 7510Pines – Package and Shipment of Environmental Samples.

7.3.4 Equipment Decontamination

All equipment that comes into contact with sediments or surface water (e.g., scoops) should be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Equipment protocol before moving to the next location. Dedicated or disposable equipment does not need to be decontaminated.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding sample collection should be documented in several areas: the sample chain-of-custody record, sample collection record, field logbook, and sample labels. Additional information regarding each form of documentation is presented in the following paragraphs:

8.1 Sample Chain-of-Custody Record

This standard form requires input of specific information regarding each collected sample for laboratory analytical purposes, as specified in ENSR SOP No. 1007Pines – Chain-of-Custody Procedures and ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

8.2 Sample Collection Record

This form (Figure 1) requires input of specific information regarding the collection of each individual sample including sample identification, water quality parameters, collection method, and containers/preservation requirements.

8.3 Field Logbook

This logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

8.4 Sample Labels

Sample labels shall be completed at the time each sample is collected and attached to each sample container. Labels may include the information listed below.

- Project number (not project name)
- Sample number
- Sample designation
- Analysis type
- Preservative
- Sample collection date
- Sample collection time
- Sampler's name

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as field duplicate, equipment and/or field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples. These requirements should be outlined in the QAPP and FSP. Additional information regarding quality assurance sample collection relevant to surface water and sediment sampling is described below.

9.1 Field Blank/Equipment Blank Sample Collection

Field blank samples serve as a quality assurance check of equipment and field conditions at the time of sampling. Field blank samples are usually prepared by transferring analyte-free water into a clean set of sample containers, then analyzing it as a sample. Sometimes, the analyte-free water is transferred over or through the sampling device before it is placed into the sample containers. This type of field blank sample is known as an equipment blank. The FSP and QAPP contain specific information regarding the type and number of field blanks or equipment blanks required for collection.

9.2 Field Duplicate Sample Collection

Field duplicate samples are collected for the purpose of providing two sets of results for comparison. These samples are used to assess precision. To the extent possible based on available information, field duplicates will be selected at locations with the likelihood of detectable concentrations of constituents. Duplicate samples are usually prepared by splitting the sample into two sets of sample containers, then analyzing each set as a separate sample. The QAPP contains specific information regarding the type and number of duplicate samples for collection.

9.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample Collection

MS/MSDs provide information about the effect of the sample matrix on digestion and measurement methodology. For samples submitted for MS/MSD analysis, triple sample volume is generally required. The QAPP contains specific information regarding the frequency of MS/MSD samples.

10.0 REFERENCES

Code of Federal Regulations, Chapter 40 (Section 261.4(d)).

ENSR SOP No. 105Pines – Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor.

ENSR SOP No. 108Pines – Field Measurement of Turbidity.

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

ENSR SOP No. 7131Pines – Field Filtration of Water Samples for Inorganic Constituents.

ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

USEPA. 1998. Sediment Sampling Guidance. USEPA, Region I. Quality Assurance Unit Staff. Office of Environmental Measurement and Evaluation. Draft September 1998.

USEPA. 1999. Innovative Technology Verification Report: Sediment Sampling Technology, Aquatic Research Instruments Russian Peat Borer, EPA/600/R-01/010. Office of Research and Development.

FIGURE 1 – EXAMPLE SURFACE WATER AND SEDIMENT SAMPLE COLLECTION RECORD

FIELD LOG SHEET
Remedial Investigation - Pines Area of Investigation; Pines, IN
AOC II - Docket No. V-W-'04-C-784

Date ____________
Time ____________
Staff ____________
Weather ____________

Site ID	

Northing ____________
Easting ____________

Site Conditions

Description (include channel description/width, % overhead canopy, % coverage by in-stream veg.):

Field Data

Meter Type: ____________ Meter ID: ____________

	Surface	Bottom
Depth (ft)		
Temperature (deg. C)		
Sp. Conductance (uS/cm)		
Dissolved Oxygen (mg/L)		
Dissolved Oxygen (% sat)		
pH (S.U.)		
Other: Color/turbidity		

Surface water sample collection:

Type of Sample Grab ______ Pump ______ Other ______
Sample depth (cm): ______
No. of samples collected: ______
No. of samples rejected: ______ Rationale: ____________

Sheen Yes / No Odor Yes / No
Sample description (include water appearance, color, turbidity, organic debris, biota presence):

Sediment collection:

Grab penetration depth (cm): ______
RPD depth (cm): ______
Number of grabs collected: ______
Number of grabs rejected: ______ Rationale: ____________

Sheen Yes / No Odor Yes / No
Grab description (include sediment type, texture color, layering, entrained debris, biota):

Temporary Monitoring Well Installation and Groundwater Sampling by HydroPunch® Technology

SOP Number 104Pines

Revision Number: 2.0

May 2005

____
ENSR Project Manager
May 23, 2005

____
ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

ATV	All Terrain Vehicle
DO	Dissolved Oxygen
FSP	Field Sampling Plan
HASP	Health and Safety Plan
MS/MSD	Matrix Spike/Matrix Spike Duplicate
ORP	Oxydation-Reduction Potential
OSHA	Occupational Safety and Health Adminstration
PVC	Poly Vinyl Chloride
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods available for installing temporary monitoring wells by HydroPunch® technology (or other similar vendor). The use of this technology can be used for purposes such as:

- Determining the presence/absence and extent of constituents in groundwater;
- A field screening tool to aid in the placement of permanent monitoring wells; and
- Temporary placement of wells for the collection of groundwater samples and estimating groundwater flow directions.

This SOP covers groundwater sampling from temporary monitoring wells using HydroPunch® technology. Use of this sampling equipment requires use of a hydraulically-powered percussion/probing machine or a conventional drilling rig. HydroPunch® technology is usually performed by subcontractors, although rental equipment is available for use by trained operators. Equivalent methods of sampling may be used with other direct-push sampling equipment.

The HydroPunch® technology methods are applicable to unconsolidated soil/fill materials. The approximate sample depth must be known prior to installation.

2.0 SUMMARY OF METHOD

Installation of temporary monitoring wells using the HydroPunch® technology requires use of a hydraulically-powered percussion/probing machine. The percussion/probing machine is typically mounted onto the bed of a pickup truck or van so that a stable working platform is established. The percussion/probing machine, through its hydraulic operation, pushes and hammers the temporary well equipment vertically into the ground within the targeted sampling interval. The approximate sample depth must be known prior to installation, and is specified in the Field Sampling Plan (FSP). Once the desired depth is reached, the push rods are retracted exposing the filter screen allowing groundwater to infiltrate the sampling equipment (see Figure 1). At this time a groundwater sample can be collected from the temporary monitoring well. This SOP assumes yields and recharge to the sampling points are sufficient to readily yield groundwater samples.

3.0 HEALTH AND SAFETY WARNINGS

The installation of temporary monitoring wells may involve chemical hazards associated with exposure to materials in the groundwater being investigated and physical hazards associated with drilling equipment and installation methods. When the installation of temporary monitoring wells is performed, adequate health and safety measures must be taken to protect field personnel. These measures will be addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

The direct push technologies have limited downward pressure for pushing, so they cannot be used in rock or where soils are too dense. Because multiple water samples may be collected from the same borehole, there is a potential for cross-contamination between samples, especially for oily or organic constituents (not expected for this project).

Potential interferences could also result from cross-contamination between sample locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

There may also be potential interferences between the HydroPunch® sampling equipment and the samples themselves. Because the constituents to be monitored are metals and/or inorganics, plastic materials will be used in lieu of metal where possible. Glass materials will not come into contact with the samples, unless the glass is guaranteed boron and silicon free.

5.0 PERSONNEL QUALIFICATIONS

Field and subcontractor personnel will be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present. Geologists or personnel with geologic experience should supervise the temporary well installation. The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana.

It is the responsibility of field personnel to install temporary monitoring wells in a manner consistent with this SOP, with specific sampling, quality assurance, and health and safety requirements outlined within the FSP, Quality Assurance Project Plan (QAPP), and the HASP. Field personnel are responsible for collecting samples, decontamination of equipment, as well as proper documentation in the field logbook or field forms (if appropriate). It is also the field personnel's responsibility to indicate the specific targeted sampling depth or sampling interval to the subcontractor (specific sampling depths are indicated in the FSP).

It will be the responsibility of the subcontractor to provide a trained operator and the necessary HydroPunch® equipment for obtaining groundwater samples. This generally includes the truck- or all terrain vehicle (ATV)-mounted percussion/probing machine and one or more HydroPunch® samplers in good operating condition, appropriate drive points/filter screens, and other necessary equipment for installation and sampling.

6.0 EQUIPMENT AND SUPPLIES

In addition to those materials provided by the subcontractor, other field supplies may include:

- Groundwater sampling supplies (as required by ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells)
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice)
- Sample Chain-of-Custody forms (as required by ENSR SOP No. 1007Pines – Chain-of-Custody Procedures)
- Sample packaging and shipping supplies (as required by ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples)
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)
- Approved plans (e.g., QAPP, FSP, HASP)
- Field project logbook/pen

7.0 METHODS

7.1 General Method Description

HydroPunch® sampling methods generally involve collection of groundwater samples by driving the sampling tool directly into the ground using the percussion/probing machine and without the aid of hollow-stem augers or other casing-installed drilling methods. The sampler consists of a metal tube of seamless construction that can not be split apart like split-spoons. A disposable poly vinyl chloride (PVC) screen with steel drop off tip is threaded to the end of the sampling device.

The sampling device operates by being directly pushed/hammered into the ground by the percussion/probing machine. The sampling device is advanced to the desired depth within the groundwater table. The push rods are then retracted exposing the filter screen allowing groundwater to infiltrate the sampler. Where samples are to be collected from multiple depths, the sampling device continues to be advanced to the next deeper sampling interval after the collection of each sample. When the sampling device is retrieved from the ground, the push rods and sampler are retrieved, leaving the screen and steel drop off tip in the ground.

7.2 Sampling Procedures

(Note: This SOP assumes that the down-hole equipment will be handled by the subcontractor; therefore, detailed procedures regarding sample acquisition are not provided.)

7.2.1 Assemble the HydroPunch® sampler by placing the screen with steel drop off tip on the end of the sampler.

7.2.2 Thread the sampler onto the drive head.

7.2.3 Using the percussion/probing machine, drive the sampler into the ground until the drive head reaches the desired depth and is within the groundwater table.

7.2.4 Retract the push rods to expose the filter screen, allowing groundwater to infiltrate the screen.

7.2.5 Either the subcontractor or the field personnel will set up a peristaltic pump to extract groundwater from the screen. The intake point on the tubing will be set within but near the top of the screen. The pump will be operated at a relatively slow rate (less than 0.5 L/min) to minimize formation disturbance and reduce the amount of particulate material in the collected sample. A minimum of three well volumes of water will be removed from the down-hole sampler to flush any stagnant or residual water. Because screening-level data are being collected, formal purging (parameter stabilization) is not required.

7.2.6 Connect the discharge of the peristaltic pump to a flow-through cell equipped with sensors to record temperature, specific conductance, dissolved oxygen (DO), oxygen reduction potential (ORP), and pH (see ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor). Measure the turbidity (see ENSR SOP No. 108Pines – Field Measurement of Turbidity).

7.2.7 Disconnect the flow-through cell and collect groundwater samples from the discharge of the peristaltic pump according to the procedures contained in ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells.

7.2.8 If the depth to groundwater is too deep for operation of a peristaltic pump, samples may be collected using a bailer.

7.2.9 Advance the sampler to the next deepest sample interval, if appropriate.

7.2.10 Use the machine hydraulics to pull the sampler from the ground. Only the push rods and sampler will be removed, leaving the screen and drive tip in the ground.

7.3 Equipment Decontamination

All equipment that comes into contact with soil and/or groundwater (e.g., push rods, etc.) will be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment prior to use and between locations.

8.0 DATA AND RECORDS MANAGEMENT

The field logbook is kept as a general log of activities and should maintain details of the HydroPunch® well installation. Sample collection will be documented in accordance with ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as field duplicate, equipment and/or field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples. These requirements are outlined in the FSP and QAPP. Additional information regarding quality assurance sample collection relevant to groundwater sampling is described below.

9.1 Field Blank/Equipment Blank Sample Collection

Field blank samples serve as a quality assurance check of equipment and field conditions at the time of sampling. Field blank samples are usually prepared by transferring analyte-free water into a clean set of sample containers, then analyzing it as a sample. Sometimes, the analyte-free water is transferred over or through the sampling device before it is placed into the sample containers. This type of field blank sample is known as an equipment blank. The FSP and QAPP contains specific information regarding the type and number of field blanks or equipment blanks required for collection.

9.2 Field Duplicate Sample Collection

Field duplicate samples are collected for the purpose of providing two sets of results for comparison. These samples are used to assess precision. To the extent possible based on available information, field duplicates will be selected at locations with the likelihood of detectable concentrations of constituents. Duplicate samples are usually prepared by splitting the sample into two sets of sample containers, then analyzing each set as a separate sample. The QAPP contains specific information regarding the type and number of duplicate samples for collection.

9.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample Collection

MS/MSDs provide information about the effect of the sample matrix on digestion and measurement methodology. For samples submitted for MS/MSD analysis, triple sample volume is generally required. The QAPP contains specific information regarding the frequency of MS/MSD samples.

10.0 REFERENCES

ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor.

ENSR SOP No. 108Pines – Field Measurement of Turbidity.

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells.

ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

Gregg Drilling, www.greggdrilling.com. “Groundwater Sampling (GWS)”.

FIGURE 1 – HYDROPUNCH® GROUNDWATER SAMPLER

Groundwater Sampling (GWS)

Gregg In Situ, Inc. conducts groundwater sampling using a Hydropunch® type groundwater sampler, *Figure GWS*. The groundwater sampler has a retrievable stainless steel or disposable PVC screen with steel drop off tip. This allows for samples to be taken at multiple depth intervals within the same sounding location. In areas of slower water recharge, provisions may be made to set temporary PVC well screens during sampling to allow the drill rig to advance to the next sample location while the groundwater is allowed to infiltrate.

The groundwater sampler operates by advancing 1 ¾ inch hollow push rods with the filter tip in a closed configuration to the base of the desired sampling interval. Once at the desired sample depth, the push rods are retracted; exposing the encased filter screen and allowing groundwater to infiltrate hydrostatically from the formation into the inlet screen. A small diameter bailer (approximately ½ or ¾ inch) is lowered through the push rods into the screen section for sample collection. The number of downhole trips with the bailer and time necessary to complete the sample collection at each depth interval is a function of sampling protocols, volume requirements, and the yield characteristics and storage capacity of the formation. Upon completion of sample collection, the push rods and sampler, with the exception of the PVC screen and steel drop off tip are retrieved to the ground surface, decontaminated and prepared for the next sampling event.

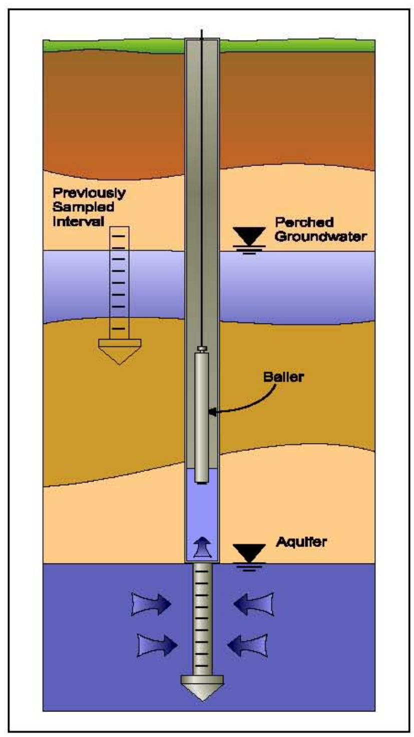

Figure GWS

For a detailed reference on direct push groundwater sampling, refer to Zemo et. al., 1992.

GREGG
2726 Walnut Avenue · Signal Hill · California · 90755 · Phone: (562) 427-6899 · Fax: (562) 427-3314
Web Site: www.greggdrilling.com Email: info@greggdrilling.com
Additional locations in: Charleston · Houston · Palo Alto · Salt Lake City · San Francisco · Vancouver

Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor

SOP Number 105Pines

Revision Number: 1.0

January 2005

Lisa A. Bradley

ENSR Project Manager
January 18, 2005

Debra L. McGrath

ENSR Project QA Officer
January 18, 2005

ENSR Corporation
January 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

DO	Dissolved Oxygen
FSP	Field Sampling Plan
HASP	Health and Safety Plan
ORP	Oxydation-Reduction Potential
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedure that will be followed by field staff for measuring water quality characteristics using a YSI-6920 or similar multi-parameter water quality meter.

Several YSI multi-parameter meters are available, including models such as 6920, 610XL and 610XLM. All are calibrated and used in the same manner. The model used for the purposes of this SOP is model YSI 6920, and equivalent procedures may be used to operate similar instruments. The multi-parameter meters are equipped with sensors for the measurement of dissolved oxygen (DO), specific conductance, temperature, pH, and oxidation-reduction potential (ORP). Data can be viewed in real-time using a hand-held data logger.

2.0 SUMMARY OF METHOD

The multi-parameter meter is used to measured water quality parameters in the field, including DO, specific conductance, temperature, pH, and ORP. These may be used to establish the sufficiency of purging prior to collecting groundwater samples from monitoring wells, or to document water quality conditions in groundwater, surface water, and/or private well water.

The multi-parameter meter may be set directly into a water body, or within a flow-through cell or other container into which the water is placed or pumped. The instrument readings are displayed on a hand-held data logger. These readings may be recorded electronically by the datalogger or transcribed to the field log book or appropriate field data form.

3.0 HEALTH AND SAFETY WARNINGS

Measuring water quality parameters may involve chemical hazards associated with materials in the water being monitored and instrument calibration solutions, and physical hazards associated with general field work. When measuring water quality parameters, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences will be controlled through appropriate calibration of the instruments, and decontamination between sample locations.

5.0 PERSONNEL QUALIFICATIONS

To properly calibrate the instrument and perform water quality measurements, the field personnel must be familiar with the calibration and measurement techniques stated in this SOP. The field personnel must also be experienced in the operation of the meter.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP and health and safety requirements outlined within the Field Sampling Plan (FSP) and HASP. Field personnel are responsible for the proper use, maintenance, and decontamination of all equipment used in the calibration and operation of the multi-parameter meter, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT SUPPLIES

6.1 YSI 6920 Multi-Parameter Meter

The following materials are necessary for calibration and operation of this instrument:

- YSI 6920 or equivalent multi-parameter meter with hand-held datalogger
- Calibration Standards
  - pH 4.0, 7.0, and 10.0 standard buffer solutions
  - Conductivity standard appropriate for field conditions expected
  - ORP calibration solution (e.g., Zobell solution)
- YSI transport cup
- YSI probe guard
- Chemical-free paper towels
- YSI DO calibration kit (electrolyte solution and Teflon® membranes)

- Ring stand and clamps suitable for holding YSI unit during calibration
- Barometer
- Calibration Form (Figure 1)

6.2 Other Required Materials

Other materials that may be required to facilitate use of the instruments in the field include:

- YSI flow-through cell, bucket, or other container(s)
- Tubing to connect multi-parameter meter to pumps (as necessary)
- Replacement batteries for the datalogger display unit
- Health and safety supplies (as required by the HASP)
- Distilled/deionized water supply
- Deionized water dispenser bottler
- Equipment decontamination materials (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

Calibration of the YSI-6920 is required to assure performance of the meter. Specific calibration solutions are use for the calibration of specific conductance, pH, and ORP. Water is used for the calibration of DO. Temperature is not calibrated but may be checked against a secondary thermometer, if necessary.

7.2 Calibration

The YSI-6920 (or equivalent) will be calibrated daily prior to use according to the requirements of the QAPP and manufacturer's specifications. It will also be checked daily with the calibration solutions at the end of use of the equipment (post-calibration). Calibration records shall be recorded in the field logbook or Calibration Form (Figure 1). The required calibration procedures are summarized below.

All instruments except temperature may require calibration. During calibration, ensure that all sensors are immersed in the standard solutions. Use recommended volumes when performing calibrations.

Rinse the probes between calibration solutions using clean ambient temperature deionized water. For maximum accuracy, follow up by pre-rinsing the probes with a small amount of the calibration solution required for the next calibration.

Have clean, absorbent, lint-free, paper towels to dry the probes between rinses and calibration solutions. It is important to remove as much residual liquid as possible from the probes after each rinse. Drying the probes in this way reduces carry-over contamination of calibration solutions and increases the accuracy of the calibration.

After powering up the YSI-6920, the Main Menu will be displayed on the data logger. To access the calibration menu select option “2-Calibrate” from the Main Menu, the unit will display all the installed sensors which necessitate a pre-calibration prior to deployment and data acquisition (i.e., specific conductance, DO, pH, and ORP). The calibration procedure for each of the sensors is explained individually below.

7.2.1 Specific Conductance Sensor

Place enough specific conductance calibration solution in the YSI transport cup so that the probe will be entirely submerged in the solution.

Select the conductivity sensor off the Calibrate Menu to access the conductivity calibration procedure, then select SpCond to access the specific conductance calibration procedure.

Enter the calibration value of the standard you are using (mS/cm at 25 ^{o}C) and press ENTER. The current values of all enabled sensors will appear on the screen and will change with time as they stabilize.

Observe the readings under SpCond and when no significant change occurs in the display for approximately 30 seconds, record the initial temperature and value in the field logbook or Calibration Form (Figure 1). Then press ENTER. The screen will indicate that the calibration has been performed successfully.

Now record the temperature, calibration value as well as date and time the calibration was performed in the field logbook or Calibration Form (Figure 1).

After the appropriate data has been recorded, the data logger will prompt you to press ENTER to return to the Calibrate Menu.

Rinse the probes in clean, deionized water and thoroughly dry.

7.2.2 DO Sensor

Place approximately 1/8” (3 mm) of water into the YSI transport cup and engage 1 or 2 threads on the probe. Make certain that the DO and temperature probes are not immersed in the water. Do not tighten; a loose connection which allows the transport cup to freely vent to the atmosphere is required to properly complete this calibration step. Wait approximately 10 minutes for the air in the calibration cup to become water saturated and for the temperatures of the thermistor and the oxygen probe to equilibrate.

Select 2-Dissolved Oxy from the Calibrate Menu, then select 1-DO% to access the DO% calibration procedure. Enter the current local barometric pressure in mm Hg (inches Hg x 25.4 = mm Hg). Do not use barometer readings obtained from meteorological reports, these are corrected to sea level and will produce an inaccurate calibration.

A countdown timer will be displayed on the lower left of the screen that allows for the proper warm up time for the DO sensor. Wait for the countdown to be completed before proceeding. A message that indicates to press ENTER to continue will appear. Pressing ENTER will return the display to the DO calibration. When the DO% values reach a stabilized value, record the initial temperature and value in the field logbook or Calibration Form (Figure 1). Then press ENTER to accept the calibration.

The temperature, calibration value as well as date and time the calibration was performed should be recorded in the field logbook or Calibration Form (Figure 1).

NOTE: Calibration of the DO sensor following the DO% procedure will simultaneously achieve calibration in the DO mg/L mode and vice versa.

7.2.3 pH Probe (3-Point Calibration)

Place the appropriate volume of pH 7.0 standard buffer solution into a pre-rinsed transport cup and allow 1 minute for temperature equilibration before proceeding. From the Calibrate Menu, select 4-ISE1 pH to access the pH calibration procedure and select 3-3-point. Press ENTER and input the value of the buffer (7.0) at the prompt. Press ENTER and the current values received from the sensors will be displayed. When the unit has stabilized and there are no significant changes for approximately 30 seconds, record the initial temperature and value in the field logbook or Calibration Form (Figure 1). Then press ENTER to accept this calibration step. Now record the temperature, calibration value as well as date and time the calibration was performed in the field logbook or Calibration Form (Figure 1).

Press ENTER to continue with the second point in the calibration procedure. Rinse the probe in water and dry thoroughly before proceeding. Select the pH 4.0 standard buffer solution and place the appropriate volume into pre-rinsed transport cup. Press ENTER and input the value of the second buffer at the prompt. Following the same procedure as above, press ENTER and the current values received from the sensors will be displayed. When the unit has stabilized and there are no significant changes for approximately 30 seconds, record the initial temperature and value in the field logbook or Calibration Form (Figure 1). Then press ENTER to accept and complete this calibration step. Now record the temperature, calibration value as well as date and time the calibration was performed in the field logbook or Calibration Form (Figure 1).

Thoroughly rinse the probe and the calibration container in water and thoroughly dry. Repeat this procedure with the pH 10.0 standard solution.

Note that once field conditions are known, it may be possible to perform a 2-point calibration using the 4.0 to 7.0 or 7.0 to 10.0 range, ensuring that the expected range of field conditions is captured.

7.2.4 ORP

Calibration is not usually required for the ORP sensor. However, for some older probes, there may be deviation from the theoretical ORP value. To check for functionality, the ORP probe is placed in Zobell solution. If the probe is functioning properly, the reading should be within the range of 221 to 241 at normal ambient temperatures. If the reading is outside this range, the probe should be calibrated.

To calibrate, select ISE2-Orp from the calibrate menu. Immerse the probe into the Zobell solution and press ENTER. Enter in the Zobell solution value. Press ENTER and monitor the stabilization of the ORP and temperature readings. After no significant change occurs for approximately 30 seconds, record the initial temperature and value in the field logbook or Calibration Form (Figure 1). Then press ENTER to confirm the calibration. Now record the temperature, calibration value as well as date and time the calibration was performed in the field logbook or Calibration Form (Figure 1).

7.3 Collection of Measurements

Attach the field cable to the probe and hand tighten – DO NOT use tools! Make sure all port plugs are installed in all port connections where probes are not installed, it is extremely important to keep these electrical connections dry. Immerse the multi-parameter meter into the water being monitored. Ensure that the YSI data logger is properly connected and in RUN mode displaying data.

<u>NOTE</u>: Do not collect data until the sensor display has stabilized, particularly the parameters of DO and pH. Allow the DO sensor to warm up from 40 to 180 seconds after being immersed on station, depending on the water temperature.

Record the displayed data on a field log sheet or in the field logbook.

7.4 Equipment Decontamination

The YSI-6920 multi-parameter meter should be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment between each sample location. Dedicated or disposable equipment does not need to be decontaminated.

Where the multi-parameter meter is used to monitor stabilization of parameter values during well purging, decontamination between locations is not needed as the purging process will effectively decontaminate the instruments as verified when parameters are stabilized.

8.0 DATA AND RECORDS MANAGEMENT

Calibration records will be recorded in the field logbook or appropriate field form. All field information will be recorded in the field logbook or on a field collection form by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the calibration process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel will follow specific quality assurance guidelines as outlined in the Quality Assurance Project Plan (QAPP) and/or FSP.

10.0 REFERENCES

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

YSI 6920 Multi-Parameter Water Quality Monitor Operations and Instructions Manual.

FIGURE 1 – Example Calibration Form

Project Name:____________________

Project Number:__________________

Date:__________________________

Calibration Form

Parameter	Instrument		Standard		Standard Value @ __C	Ambient Temp. C	Initial Value	Adjusted Value	Initials & Time	Comments
	Manf/Model	Serial No.	Manf/Model	SN/Exp. Date						
pH 4.00	YSI 6920				4.00 @ 25C					
								----------		Post Cal
pH 7.00					7.00 @ 25C					
								----------		Post Cal
pH 10.00					10.00 @ 25C					
								----------		Post Cal
Specific Cond.					_____uS/cm @ 25C					
								----------		Post Cal
ORP					_____mV @ _____C					
								----------		Post Cal
DO			H2O Saturated Air		_____mg/L @ _____C					BP =
								----------		Post Cal; BP =

BP = Barometric Pressure (mmHg)

Sample Collection from Private Wells

SOP Number 106Pines

Revision Number: 2.0

May 2005

Lisa A. Bradley

ENSR Project Manager
May 23, 2005

Debra L. McGrath

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

DO	Dissolved Oxygen
FSP	Field Sampling Plan
HASP	Health and Safety Plan
MS/MSD	Matrix Spike/Matrix Spike Duplicate
ORP	Oxygen Reduction Potential
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operation Procedure (SOP) describes the method for collecting valid and representative samples from private water supply wells, typically domestic wells at residential households.

2.0 SUMMARY OF METHOD

Sampling of private wells generally involves opening an existing spigot or tap on the water distribution system within a residence. Prior to sample collection, the water should be run for several minutes to flush stagnant water from the system.

3.0 HEALTH AND SAFETY WARNINGS

Although there are no unusual hazards associated with sampling private wells, all work will be conducted in accordance with the project Health and Safety Plan (HASP).

4.0 INTERFERENCES

Potential interferences could result when the groundwater pumped from the subsurface by the household pump comes in contact with the distribution system, including any treatment. These potential interferences will be minimized by allowing water to run prior to sample collection, selection of a sampling location that minimizes contact with the distribution system, and ensuring that samples are collected prior to any treatment system. If a sample cannot be collected prior to a treatment system, no sample will be collected.

5.0 PERSONNEL QUALIFICATIONS

Collecting private well samples is a relatively simple procedure requiring minimal training and a relatively small amount of equipment. It is recommended that the personnel collecting private wells samples have some previous experience in this activity or be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field sampling personnel to be familiar with the sampling procedures outlined within this SOP, and with specific sampling, quality assurance, and health and safety requirements outlined in the Field Sampling Plan (FSP), Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for collecting private well samples, decontamination of equipment (as appropriate), as well as proper documentation of sampling activities in the field logbook or field forms (as appropriate).

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Field Instruments - Individual or multi-parameter meter(s) to measure temperature, pH, specific conductance, dissolved oxygen (DO) oxidation reduction potential (ORP), and/or turbidity
- Hose or tubing
- Sample Collection Records (Figure 1)
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice)
- Sample Chain-of-Custody forms (as required by ENSR SOP No. 1007Pines – Chain-of-Custody Procedures)
- Sample packaging and shipping supplies (as required by ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples)
- Waterproof marker or paint
- Distilled/deionized water supply
- Deionized water dispenser bottler
- Buckets
- Instrument calibration solutions
- Paper towels
- Trash bags
- Zipper-lock bags
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)
- Approved plans (e.g., HASP, QAPP, FSP)
- Field logbook/pen

7.0 METHODS

7.1 Instrument Calibration

Field instruments will be calibrated daily according to the requirements of the manufacturer's specifications for each piece of equipment (e.g., ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor). Equipment will also be checked daily with the calibration solutions at the end of use of the equipment. Calibration records shall be recorded in the field logbook or appropriate field form.

7.2 Access and Well Information

Private wells are owned and maintained by individuals on property not under control of the Respondents. It is the responsibility of the Remedial Investigation Task Manager to ensure that permission for sampling of private wells has been received from the property owner or other responsible party, and that the owner has been contacted concerning the proposed date and time of the sampling. It is the responsibility of the field personnel to verify this information prior to sampling, and to contact the owner if the sampling schedule is changed.

Prior to sampling at each location, a formal well survey will be conducted. The well owner will be interviewed to obtain any available information about well location, depth, and construction, and information about the water distribution in the house so that an appropriate sample location can be selected. The results of the well survey will be documented on the Sample Collection Form (Figure 1) and/or in the field logbook.

7.3 Selection of Sample Point

Within the residence, a location along the existing water distribution system must be selected from which the sample will be collected. All taps or spigots are potential sampling locations. The sample location will be selected at the spigot within the house as close to the wellhead as possible. Ideally, the first tap or spigot will be located on the system as soon as the piping enters the house. If this is not possible, the following criteria will be considered:

- In no case will the sample be collected from the hot water piping (i.e., after a hot-water heater or other heating system).

- In no case will the sample be collected after a treatment system.

- Locations at spigots in the piping are preferred over taps at sinks, as many taps may include aeration, filters, or other features. If possible, these may be removed prior to sampling. An outdoor spigot or utility sink is less likely to have these features.

- As the water will be run for several minutes prior to sampling, a location near a sink or drain is more convenient (but not required).

If a sample location meeting these criteria cannot be identified, then no sample will be collected. The location of the selected sample point will be documented in the field logbook. If no sample is collected from a particular private well, the reason must be documented on a Field Change Order (see ENSR SOP No. 100 - Field Change Order Procedures).

7.4 Well Purging

Prior to sample collection, the water will be run for approximately 15 minutes to flush stagnant water out of the piping. The water may be run from the sampling point directly into a sink or drain, or piped to a sink or drain using hose or tubing. If there is no drain or sink convenient to the sample location, the water can be run from any tap in the house. The well owner's convenience should be consulted about this process.

The purging process, including duration and estimated rate of flow, will be documented on the Sample Collection Form (Figure 1) and/or in the field logbook. Flow rates will be estimated by measuring the amount of water discharged over 1 minute into a marked flow-cup.

7.5 Measurement of Field Parameters

At the completion of the purging process, field parameters of the pumped water will be measured. Parameters will be measured at the sample point by pumping water from the sampling point into a flow-cup or other decontaminated, plastic container. The following parameters will be measured: pH, specific conductivity, temperature, DO, and ORP. These parameters will be measured with a water quality meter, calibrated according to the manufacturer's specifications (e.g., ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor). Turbidity will be measured separately with a nephelometer, also calibrated to the manufacturer's specifications (see ENSR SOP No. 108Pines - Field Measurement of Turbidity). The results will be documented on the Sample Collection Form. For private well sampling, it is not necessary to establish stabilization of these parameters.

Water from the flow-cup may be discharged directly to a nearby sink or drain. If there is no sink or drain convenient to the sample location, the discharge water will be contained in a bucket and carried to a sink at the completion of sampling.

7.6 Sample Collection

Once the field parameters are measured and recorded, water from the sampling point will be used to fill the appropriate bottleware supplied by the laboratory. Water will continue to be run from the sampling point continuously, without turning off the water between bottles. It may be convenient for this to take place over a sink, drain, or bucket.

7.7 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.
- Cap and label the container with (at a minimum) the sample identifier and sampling date and time. Additional information such as preservation information and analytical tests will also be added to the sample label as appropriate. Sample labeling will be conducted per the FSP and QAPP.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.
- Package the samples for shipment to the laboratory per ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

7.8 Equipment Decontamination

Typically, no equipment decontamination is needed after private well sampling, because all materials are disposable or dedicated (e.g., the household water distribution system).

However, any necessary decontamination will be performed in accordance with ENSR SOP No. 7600Pines – Decontamination of Equipment.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding sample collection should be documented in several areas: the sample chain-of-custody record, field logbook, and sample labels. Additional information regarding each form of documentation is presented in the following paragraphs:

8.1 Sample Chain-of-Custody Record

This standard form requires input of specific information regarding each collected sample for laboratory analytical purposes, as specified in ENSR SOP No. 1007Pines – Chain-of-Custody Procedures and ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

8.2 Sample Collection Record

This form (Figure 1) requires input of specific information regarding the collection of each individual sample including sample identification, water quality parameters, collection method, and containers/preservation requirements.

8.3 Field Logbook

This logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

8.4 Sample Labels

Sample labels shall be completed at the time each sample is collected and attached to each sample container per the FSP and QAPP. Labels may include the information listed below.

- Project number (not project name)
- Sample number
- Sample designation
- Analysis type
- Preservative
- Sample collection date
- Sample collection time
- Sampler's name

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as field duplicate, equipment and/or field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples. These requirements are outlined in the FSP and QAPP. Additional information regarding quality assurance sample collection relevant to groundwater sampling is described below.

9.1 Field Blank/Equipment Blank Sample Collection

Field blank samples serve as a quality assurance check of equipment and field conditions at the time of sampling. Field blank samples are usually prepared by transferring analyte-free water into a clean set of sample containers, then analyzing it as a sample. Sometimes, the analyte-free water is transferred over or through the sampling device before it is placed into the sample containers. This type of field blank sample is known as an equipment blank. The FSP and QAPP contain specific information regarding the type and number of field blanks or equipment blanks required for collection.

9.2 Field Duplicate Sample Collection

Field duplicate samples are collected for the purpose of providing two sets of results for comparison. These samples are used to assess precision. To the extent possible based on available information, field duplicates will be selected at locations with the likelihood of detectable concentrations of constituents. Duplicate samples are usually prepared by splitting the sample into two sets of sample containers, then analyzing each set as a separate sample. The QAPP contains specific information regarding the type and number of duplicate samples for collection.

9.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample Collection

MS/MSDs provide information about the effect of the sample matrix on digestion and measurement methodology. For samples submitted for MS/MSD analysis, triple sample volume is generally required. The QAPP contains specific information regarding the frequency of MS/MSD samples.

10.0 REFERENCES

Code of Federal Regulations, Chapter 40 (Section 261.4(d)).

ENSR SOP No. 100Pines - Field Change Order Procedures.

ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor.

ENSR SOP No. 108Pines - Field Measurement of Turbidity

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

FIGURE 1 – EXAMPLE OF PRIVATE WELL QUESTIONAIRE AND SAMPLE FORM

PRIVATE WELL QUESTIONAIRE AND SAMPLE FORM
Remedial Investigation - Pines Area of Investigation, Pines, IN
AOC II - Docket No. V-W-'01-C-784

Date: ____________ **Time:** ______________ **Staff:** ________________
Weather: __________________________

Well Survey
Name of person(s) interviewed: ______________________________
Contact info of person interviewed (phone #, etc.): ______________________________

Location/Address: ______________________________
____

Well construction information:
Location: ______________________________
____

Date installed: ____________ Driller: ____________ Depth: ____________

Well materials/construction (circle):

PVC Steel Open Borehole Other

If other, describe: ______________________________

Pump Intake Depth: ____________________

Are copies of well records available from the homeowner? Yes No

Is the water treated? Yes No
If yes, where is the treatment system? ______________________________
Describe system: ______________________________
Which taps affected: ______________________________

Sketch of water distribution system from entry point, filter, etc. Indicate sample collection point.

Signature: ______________________ Date: ______________________

Page 1 of 2

PRIVATE WELL QUESTIONAIRE AND SAMPLE FORM
Remedial Investigation - Pines Area of Investigation, Pines, IN
AOC II - Docket No. V-W-'01-C-784

Date: ______________ **Time:** ________________ **Staff:** ____________________
Weather: ______________________________
Location/Address: ____
____

Other observations and notations:

Sample Collection
Field Testing Equipment: Make Model Seriel Number

____
____

Time	pH (s.u.)	Temp. (C)	Spec. Cond (uS/cm)	D.O. (mg/L)	ORP (millivolts)	Turbidity (NTU)	Color	Other

Sample Location: ____

Estimated flow rate: ______________________ Duration of purging: ____________________

Sample ID	Container Type	No. of Containers	Preservation	Analysis	Date	Time

Signature: ______________________________ Date: ____________________________

ENSR INTERNATIONAL

Field Measurement of Turbidity

SOP Number 108Pines

Revision Number: 1.0

January 2005

ENSR Project Manager
January 18, 2005

ENSR Project QA Officer
January 18, 2005

ENSR Corporation
January 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
NIST	National Institute of Standards
NTU	Nephelometric Turbidity Unit
QAPP	Quality Assurance Project Plan
OSHA	Occupational Safety and Health Administration
SOP	Standard Operating Procedure
USEPA	U. S. Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) provides basic instructions for routine calibration and operation of nephelometers or turbidity meters to measure turbidity (e.g., such as the HF Scientific Model DFT 15CE). This SOP is designed specifically for the measurement of turbidity in accordance with U.S. Environmental Protection Agency (USEPA) Method 180.1 and Standard Methods 2130 B which address turbidity measurements for drinking water, surface water and groundwaters, and saline waters.

2.0 SUMMARY OF METHOD

Turbidity is a measure of the clarity of the water being monitored. Turbidity data can be used to establish sufficiency of well purging prior to groundwater sampling, or provide general water quality information for any water being monitored.

For this project, turbidity will be measured in a separate container, not using a multi-parameter meter placed in a flow-through cell.

3.0 HEALTH AND SAFETY WARNINGS

Measuring turbidity may involve chemical hazards associated with materials in the water being monitored and instrument calibration solutions, and physical hazards associated with general field work. The health and safety considerations will be addressed in the site-specific Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences will be controlled through appropriate calibration of the instruments, and decontamination between samples.

5.0 PERSONNEL QUALIFICATIONS

To properly perform turbidity measurements, the analyst must be familiar with the calibration and measurement techniques stated in this SOP. The analyst must also be experienced in the operation of the meter.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP and within the Field Sampling Plan (FSP), the Quality Assurance Project Plan (QAPP) and the health and safety requirements outlined HASP. Field personnel are responsible for the proper use, maintenance, and decontamination of all equipment used in the calibration and operation of the turbidity meter, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT SUPPLIES

6.1 Nephelometer/turbidity meter

The following materials are necessary for this procedure:

- Turbidity meter
- Turbidity meter manufacturer's instruction manual
- Turbidity-free water
- Clean, scratch-free sample tubes
- Formazin or polymer-based calibration standards
- Lint-free tissues
- National Institute of Standards and Technology (NIST)-traceable check standard
- Calibration/field data sheets and/or field logbooks/pen

6.2 Other Required Materials

Other materials that may be required to facilitate use of the instruments in the field include:

- Flow cup, bucket, or other container(s)
- Replacement batteries
- Health and safety supplies (as required by the HASP)
- Distilled/deionized water supply
- Deionized water dispenser bottler

- Equipment decontamination materials (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 Calibration Procedures

7.1.1 The turbidity meter must be calibrated daily before any analyses are performed. The check standard reading should be within the acceptance limits specified in the QAPP. It will also be checked daily with the calibration solutions at the end of use of the equipment (post-calibration).

Calibration records shall be recorded in the field logbook or a calibration form. Calibration documentation must be maintained in a thorough and consistent manner. At a minimum, the following information must be recorded:

- Date and time of calibration
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Expiration dates and batch numbers for all standards
- Reading for calibration standard before and after meter adjustment
- Comments

7.1.2 Follow the manufacturer's operating instructions for calibrating the turbidity meter.

7.1.3 Place check standards into clean, scratch-free sample tubes. Wipe the tube with a lint-free cloth and insert the tube into the analysis chamber.

7.1.4 Follow the manufacturer's operating instructions for reading samples.

7.1.5 Verify the calibration at the end of the day with a check standard (post-calibration). The check standard reading should be within the acceptance limits specified in the QAPP.

7.2 Collection of Measurements

7.2.1 Follow the manufacturer's operating instructions for operating the turbidity meter.

7.2.2 Place water samples into clean, scratch-free sample tubes. Wipe the tube with a lint-free cloth and insert the tube into the analysis chamber.

7.2.3 Follow the manufacturer's operating instructions for reading samples.

7.2.4 Sample turbidity results in Nephelometric Turbidity Units (NTUs) will be recorded on the appropriate field data sheets or logbooks. Turbidity readings should be recorded as follows:

Turbidity Range NTU	Report to the Nearest NTU
0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

7.2.5 Documentation for recorded data must include a minimum of the following

- Date and time of analysis
- Signature or initials of person performing the measurement
- Instrument identification number/model
- Sample identification/station location
- Comments

7.3 Equipment Decontamination

The turbidity meter should be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment between each sample. Dedicated or disposable equipment does not need to be decontaminated.

8.0 DATA AND RECORDS MANAGEMENT

Calibration records will be recorded in the field logbook or appropriate field form. All field information will be recorded in the field logbook or on a field collection form by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the calibration and measurement process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel will follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

10.0 REFERENCES

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

Methods for the Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised 1983.

ENSR INTERNATIONAL

Split Spoon Sampling for Geologic Logging

SOP Number 109Pines

Revision Number: 2.0

May 2005

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CONTENTS

LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDEM	Indiana Department of Environmental Management
OSHA	Occupational Safety and Health Adminstration
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
SPT	Standard Penetration Test
USCS	Unified Soil Classification System
USDA	United States Department of Agriculture

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods used to obtain subsurface soil samples for geologic logging and physical characterization. Subsurface soil samples are obtained in conjunction with soil boring programs, and provide information on the physical and/or chemical makeup of the subsurface environment.

The purpose of this SOP is to provide a description of a specific method or procedure to be used in the collection of subsurface soil samples. Subsurface soil is defined as unconsolidated material that may consist of one or a mixture of the following materials: sand, gravel, silt, clay, peat (or other organic soils), and/or fill material. Subsurface soil sampling conducted in accordance with this SOP will promote consistency in sampling and provide a basis for sample representativeness.

This SOP covers subsurface soil sampling by split-spoon only.

2.0 SUMMARY OF METHOD

Split-spoon subsurface soil sampling generally requires use of a drilling rig and, typically, the hollow-stem auger or other common drilling method to generate a borehole in which to use the split-spoon sampler. The split-spoon sampler is inserted through the augers (or other type of drill casing) and then driven into the subsurface soil with a weighted hammer. The sampler is then retrieved and opened to reveal the recovered soil sample. Soil samples may be collected at continuous intervals or at pre-selected vertically spaced intervals within the borehole.

3.0 HEALTH AND SAFETY WARNINGS

Subsurface soil sampling may involve chemical hazards associated with exposure to the constituents potentially present in the subsurface and physical hazards associated with use of drilling equipment. When subsurface soil sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between samples or sample locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

5.0 PERSONNEL QUALIFICATIONS

Soil sampling by split-spoon requires a moderate degree of training and experience as numerous drilling situations may occur that will require field decisions to be made. It is recommended that inexperienced personnel be supervised for several drilling locations before working on their own. Geologists or personnel with geologic experience should supervise drilling activities. The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana.

Field and subcontract personnel will be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It will be the responsibility of field personnel to ensure that subsurface soil sampling is conducted in a manner that is consistent with this SOP. Field personnel will observe all activities pertaining to subsurface soil sampling to ensure that the SOP is followed, and to record all pertinent data onto a boring log and/or field logbook. It is also the field personnel's responsibility to indicate the specific targeted sampling depth or sampling interval to the drilling subcontractor. Field personnel are also responsible for preparing a geologic description of the soils once the sampling device has been retrieved and opened. Field personnel are responsible for compiling a detailed log of the geologic materials encountered.

It will be the responsibility of the drilling subcontractor to provide a trained operator and the necessary materials for obtaining subsurface soil samples. This generally includes one or more split-spoon samplers in good, operating condition. It is the drilling subcontractor's responsibility to provide and maintain their own boring logs if desired.

6.0 EQUIPMENT AND SUPPLIES

In addition to those materials provided by the subcontractor, other field supplies include:

- Boring Log Forms (Figure 1)
- Plastic sheeting
- Trash bags
- Folding rule or tape measure
- Utility knife
- Equipment decontamination materials (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by HASP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 General Method Description

Split-spoon sampling devices are typically constructed of steel and are most commonly available in lengths of 18 and 24 inches and diameters of 1.5 to 3 inches. The split-spoon consists of a tubular body with two halves that split apart lengthwise, a drive head on the upper end with a ball-check valve for venting, and a hardened steel cutting shoe at the bottom. The soil sample enters the split-spoon through the cutting shoe as the device is driven into the ground. A replaceable plastic or metal basket is often inserted into the shoe to assist with retaining samples. Once the sampler is retrieved, the drive head and cutting shoes are removed and the split-spoon halves are then separated, revealing the sample.

Sample depth intervals are defined in the Field Sampling Plan (FSP). For this project, continuous split-spoon samples will be collected to enable development of detailed geologic boring logs.

7.2 General Procedures – Borehole Preparation

7.2.1 Advancing Casing/Augers

Soil borings that are completed for soil sampling purposes are typically advanced using hollow-stem augers and sometimes drive-and-wash or other casing methods, operated by a qualified subcontractor. The casing/augers must be of sufficient diameter to allow for soil sampling at a minimum. If hollow-stem augers are used, a temporary plug shall be used in the lead auger to prevent the auger from becoming filled with drill cuttings while drilling is in progress.

7.2.2 Obstructions

For those borings that encounter obstructions, the casing/augers will be advanced past or through the obstruction if possible. Caution should be exercised when obstructions are encountered and an effort made to identify the obstruction before drilling is continued. If the obstruction is not easily drilled through or removed, the boring should be relocated to an adjacent location, in consultation with the ENSR Remedial Investigation (RI) Task Manager. Such changes will be documented in accordance with ENSR SOP No. 100Pines – Field Change Order Procedures.

7.2.3 Use of Added Water

The use of added or recirculated water during drilling is permitted when necessary, for example, to control running sands. Based on previous experience at Yard 520, running sands, when encountered, are typically controlled by maintaining a head of water in the augers. Use of extraneous water should be minimized or avoided if possible because it may impact sample quality. Only potable water will be used, and water usage should be documented in the field logbook. Sampling and analysis of added or recirculated water may be required for quality assurance purposes. If a well is installed within the completed borehole, removal of the added water through well development is required (refer to ENSR SOP No. 7221Pines – Monitoring Well Development).

7.3 Split Spoon Sampling Procedure

7.3.1 Standard Penetration Test

The drilling subcontractor will lower the split-spoon into the borehole. Samples are generally obtained using the Standard Penetration Test (SPT) in accordance with American Society for Testing and Materials (ASTM) standards (ASTM D 1586-84). Following this method, the sampler will be driven using the 140-pound hammer with a vertical free drop of 30 inches using two turns of the rope on the cathead (or equivalent). The number of hammer blows required for every 6 inches of penetration will be recorded on the boring log by the field personnel. Blowcount information is used as an indicator of soil density for geotechnical as well as stratigraphic logging purposes. Once the split-spoon has been driven to its fullest extent, or to refusal, it will be removed from the borehole.

7.3.2 Sample Recovery

Sample recovery will be determined by field personnel who will examine the soil core once the sampler is opened. The length of sample shall then be measured with a folding rule or tape measure and recorded in the field logbook or boring log. Any portion of the split-spoon contents that are not considered part of the true sample (e.g., heaved soils) will be discarded.

7.4 Sample Logging

Geologic materials recovered from boreholes will be logged in accordance with the Unified Soil Classification System (USCS) protocols (see, for example, USEPA, 1991). Geologic descriptions will be entered on a boring log (see Figure 1). Specific information to be recorded on the log may include:

- Location identification and/or description
- Drilling subcontractor
- Geologist/field personnel name
- Drilling date
- Drilling equipment
- Split-spoon sample interval
- Blow counts
- Total depth of boring

Additional geologic description information to be recorded may include:

- Moisture content
- Color
- Grain-size
- Sorting
- Density
- Plasticity
- Other relevant observations

In accordance with Indiana Department of Environmental Management (IDEM) guidance (IDEM, 1988), additional information may also be recorded, such as U.S. Department of Agriculture (USDA) soil classification, rounding, effervescence, mineralogy, and bedding. Additional information concerning geologic logging protocols is attached to this SOP.

7.5 Equipment Decontamination

All equipment that comes into contact with soil and/or groundwater (e.g., drill rig, split-spoon) will be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment before moving to the next location.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding the split spoon sample collection should be documented in the boring log and field logbook. Additional information regarding each form of documentation is presented in the following paragraphs:

8.1 Boring Log

This form (Figure 1) will be used to record the geologic description of the split spoon samples collected. Logging protocols are attached to this SOP. Geologic logs will be reviewed by a geologist licensed to practice in Indiana.

8.2 Field Logbook

This logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana. Boring logs will be reviewed by the licensed Indiana geologist.

10.0 REFERENCES

ASTM D 1586-84. 1992. “Test Method for Penetration Test and Split-Barrel Sampling of Soils”.

ENSR SOP No. 100Pines – Field Change Order Procedures.

ENSR SOP No. 7221Pines – Monitoring Well Development.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

IDEM. 1988. Technical Guidance Document, Volume 1 – Requirements for Describing Unconsolidated Deposits. Indiana Department of Environmental Management. Draft, Revised November 18, 1988.

USEPA. 1991. Description and Sampling of Contaminated Soils: A Field Pocket Guide. EPA/625/12-91/002. November 1991.

FIGURE 1 – EXAMPLE SUBSURFACE SOIL BORING LOG

Project: Town of Pines	**Boring / Well No.:**	ENSR
Description of Location:	**Project No.:** 01776-020	ENSR Corporation 27755 Diehl Road Warrenville, IL 60555
GPS:	**Date:**	

Elevation (ft)	Depth (ft)	U.S.C.S.	Sample Recovery (inches)	Density (SPT)	Lithologic Description	Well Construction	Remarks (Sample time, sample depth, etc.)
0	0				Ground Surface		
-1	1						
-2	2						
-3	3						
-4	4						
-5	5						
-6	6						
-7	7						
-8	8						
-9	9						
-10	10				End of Boring		

Drilling Contractor:
Drilling Method:
Staff / Geologist:
Sampling Method:

Sheet: 1 of 1

ENSR INTERNATIONAL

Chain-of-Custody Procedures

SOP Number 1007Pines

Revision Number: 4.0

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LIST OF ACRONYMS

COC	Chain-of-Custody
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes chain-of-custody (COC) procedures applicable to ENSR sampling and analysis programs.

2.0 SUMMARY OF METHOD

The National Enforcement Investigations Center of the U.S. Environmental Protection Agency (USEPA) defines custody of evidence in the following manner:

- It is in your actual possession;
- It is in your view, after being in your physical possession;
- It was in your possession and then you locked or sealed it up to prevent tampering; or
- It is in a secure area.

Samples are physical evidence and should be handled according to certain procedural safeguards described in of this SOP.

3.0 HEALTH AND SAFETY WARNINGS

Not applicable.

4.0 INTERFERENCES

Not applicable.

5.0 PERSONNEL QUALIFICATIONS

Individuals responsible for completing COC documentation must be personnel working on the specific field program, have read this SOP, and have worked under the oversight of experienced personnel.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Sample Labels

- COC Form (Figure 1)
- COC Tape (Figure 2)
- Field project logbook/pen

7.0 METHODS

7.1 Field Custody

7.1.1 The field personnel is required to complete the following information on the COC form (Figure 1):

- Project Number (not project name)
- Project Location
- Field Sample Identification Number
- Date and Time of Sample Collection
- Sample Matrix
- Preservative
- Analysis Requested
- Sampler's Signature
- Signature of Person Relinquishing Sample Custody
- Date and Time Relinquished
- Sampler Remarks
- COC Tape Number

7.1.2 The COC must be filled out completely and legibly in ink. Corrections will be made, if necessary, by drawing a single line through and initialing and dating the error. The correct information is then recorded with indelible ink. All transfers from field personnel to laboratory personnel are recorded on the COC form in the "Relinquished By" and "Received By" sections.

7.1.3 If samples are to be shipped by overnight commercial courier (e.g., Federal Express), the field personnel must complete a COC form for each package (e.g., cooler) of samples and place a copy of each completed form inside the associated package before the package is sealed. Each completed COC form must accurately list the sample identification numbers of the samples with which it is packaged, and must contain the identification number of the COC tape on the package. It is not necessary for the shipping company to sign the COC.

Sample packaging will be conducted in accordance with ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

7.1.4 If samples are hand carried to a laboratory, the person hand carrying the samples is the sample custodian. If the carrier is a different person than the one who filled out the COC form and packaged the samples, then that person must transfer custody to the carrier by signing and dating each form in the "Relinquished By" section. The carrier must then sign and date each form in the adjacent "Received By" section. When the carrier transfers the samples to the laboratory, he or she must sign and date each form in the next "Relinquished By" section, and the laboratory sample custodian must sign and date each form in the adjacent "Received By" section.

7.2 Laboratory Sample Receipt and Inspection

7.2.1 Upon sample receipt, the coolers or packages are inspected for general condition and the condition of the COC tape. The coolers or boxes are then opened and each sample is inspected for damage.

7.2.2 Sample containers are removed from packing material and sample label field identification numbers are verified against the COC form.

7.2.3 The following information is recorded in the laboratory's records:

- Airbill Number
- Presence/absence of COC forms and COC tape
- Condition of samples
- Discrepancies noted
- Holding time and preservatives
- Sample storage location

7.2.4 The COC form is completed by signing and recording the date and time of receipt.

7.2.5 The ENSR Project Manager or designate must be notified of any breakage, temperature exceedances, or discrepencies between the COC paperwork and the samples.

8.0 DATA AND RECORDS MANAGEMENT

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion, and in the files of the laboratories that have performed the sample analyses.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

The records generated in this procedure are subject to review during data validation, in accordance with the Quality Assurance Project Plan (QAPP).

10.0 REFERENCES

ENSR SOP No. 7510Pines - Packaging and Shipment of Environmental Samples.

FIGURE 1 EXAMPLE CHAIN OF CUSTODY FORM

M901376

ENSR

CHAIN OF CUSTODY RECORD

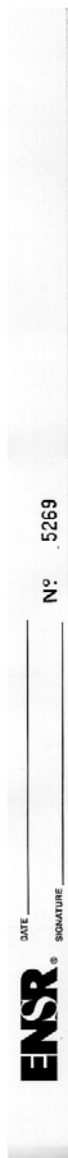
Page ____ of ____

Client/Project Name:	Project Location:	Analysis Requested
Project Number:	Field Logbook No.:	
Sampler: (Print Name) /Affiliation: Signature:	Chain of Custody Tape No.: Send Results/Report to:	

Field Sample No./ Identification	Date	Time	Grab	Comp	Sample Container (Size/Mat'l)	Sample Type (Liquid, Sludge, Etc.)	Preservative	Field Filtered							Lab I.D.	Remarks

Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	Analytical Laboratory (Destination): ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	
Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	Serial No.

FIGURE 2 EXAMPLE CHAIN OF CUSTODY TAPE



Subsurface Soil Sampling by Geoprobe^{TM} Methods

SOP Number 7116Pines

Revision Number: 1.0

December 2004

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December 23, 2004

ENSR Project QA Officer
December 23, 2004

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CONTENTS

LIST OF ACRONYMS

CCBs	Coal Combustion By-Products
HASP	Health and Safety Plan
IDW	Investigation-derived Waste
MS/MSDs	Matrix spike/matrix spike duplicates
OSHA	Occupational Safety and Health Adminstration
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods available for collecting subsurface soil samples using commercially available Geoprobe™ Systems (or other similar vendor) soil probing equipment. Subsurface soil samples may be obtained using this system for purposes of observing subsurface soil conditions and for obtaining soil samples for physical and/or chemical evaluation.

The purpose of this SOP is to provide a description of a specific method or procedure to be used in the collection of subsurface soil samples using the Geoprobe™ system. Subsurface soil is defined as unconsolidated material which may consist of one or a mixture of the following materials: sand, gravel, silt, clay, peat (or other organic soils), fill material, and coal combustion by-products (CCBs). Subsurface soil sampling, conducted in accordance with this SOP will promote consistency in sampling and provide a basis for sample representativeness.

This SOP covers subsurface soil sampling using Geoprobe™ Systems equipment; specifically, the Macro-Core Sampler for soil. Use of this sampling equipment requires use of the Geoprobe™ hydraulically-powered percussion/probing machine. Geoprobe™ sampling is usually performed by subcontractors, although rental equipment is available for use by trained operators. Equivalent methods of sampling may be used with other direct-push sampling equipment.

The Geoprobe™ sampling methods covered in this SOP are applicable to unconsolidated soil/fill materials and to a maximum recommended depth of approximately 30 feet. Sampling depths are greatly dependent upon soil density as the hydraulically-powered probing unit has power limitations. Sample recovery is also somewhat dependent on grain size as very coarse gravel, cobbles, and boulders will occasionally cause premature refusal of the sampler.

2.0 SUMMARY OF METHOD

Soil sampling using the Geoprobe™ System requires use of the hydraulically-powered percussion/probing machine and the Macro-Core Soil Sampler sampling devices. The percussion/probing machine is typically mounted onto the bed of a pickup truck or van so that a stable working platform is established. The percussion/probing machine, through its hydraulic operation, pushes and hammers the soil sampling equipment (Macro-Core Sampler) vertically into the ground within the targeted sampling interval. The soil sampler is then extracted from the ground to recover the sample.

The Macro-Core Sampler (Figure 1) consists of a 45-inch long by 1.5-inch diameter open-ended steel sampling tool with liners made of Teflon®. The tool is designed for use in a continuous sampling capacity in an open borehole up to depths of approximately 30 feet. The borehole walls are required to stay open in order to collect a sample from the next depth interval. Once the sampling tool is removed from the ground, the inserted liner containing the soil sample is removed from the tool. The soil sample is then cut from or extracted from the liner. This sampling tool is most often used for soil profiling and collection of larger volume soil samples (1,300 ml).

3.0 HEALTH AND SAFETY WARNINGS

Subsurface soil sampling may involve chemical exposure hazards associated with the type of constituents present in subsurface soil. When subsurface soil sampling is performed, adequate Health and Safety measures must be taken to protect sampling personnel. These measures will be addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between samples or sample locations. Minimization of the cross contamination will occur through the following:

- The use of clean sampling tools at each location as necessary.
- Avoidance of material that is not representative of the media to be sampled. Material that has been in contact with the Geoprobe™ will not be sampled.

5.0 PERSONNEL QUALIFICATIONS/RESPONSIBILTIES

Sampling personnel will be health and safety certified as specified by OSHA (29 CFR 1910.120(e)(3)(i)) to work on this project in accordance with the HASP.

It will be the responsibility of the project geologist/sampling engineer to conduct subsurface soil sampling in a manner which is consistent with this SOP. The project geologist/sampling engineer will observe all activities pertaining to subsurface soil sampling to ensure that the SOP is followed, and to record all pertinent data onto a boring log and/or field logbook. It is also the project geologist/sampling engineer's responsibility to indicate the specific targeted sampling depth or sampling interval to the drilling subcontractor. The project geologist/sampling engineer is also responsible for the collection of representative environmental or stratigraphic characterization samples once the sampling device has been retrieved and opened. Additional sample collection responsibilities include labeling, handling, and storage of samples until further chain-of-custody procedures are implemented.

It will be the responsibility of the drilling subcontractor to provide the necessary Geoprobe™ equipment for obtaining subsurface soil samples. This generally includes the truck or ATV-mounted percussion/probing machine and one or more Macro-Core Samplers in good operating condition, appropriate liners, and other necessary equipment for borehole preparation and sampling. It is the drilling subcontractor's responsibility to provide and maintain their own boring logs if desired. Equipment decontamination materials should also be provided by the subcontractor and should meet project specifications.

6.0 EQUIPMENT AND SUPPLIES

In addition to those materials provided by the subcontractor, the project geologist/sampling engineer will require:

- Boring Logs
- Spoons or scoops
- Sample kit (bottles, labels, custody records and tape, cooler, ice)
- Sample collection pan
- Folding rule or tape measure
- Utility knife
- Equipment decontamination materials (as required by ENSR SOP 7600Pines – Decontamination of Field Equipment)
- Health and safety equipment (as required by HASP)
- Field project notebook/pen

Sampling equipment which comes in direct contact with environmental samples during sample collection under the Yard 520 Sampling and Analysis Plan (SAP) should be constructed of Teflon®. Other plastics and metal are to be avoided to minimize potential artifacts in the analyses.

7.0 METHODS

7.1 General Method Description

Geoprobe™ soil sampling methods generally involve collection of soil samples by driving the sampling tool directly into the ground using the percussion/probing machine and without the aid of hollow-stem augers or other casing-installed drilling methods. The Macro-Core Sampler consists of a metal tube of seamless construction which can not be split apart like split-spoons. Liner/sleeve inserts are required in order to extract an intact soil core/sample from the sampling device.

The sampling device operates by being directly pushed/hammered into the ground by the percussion/probing machine. The borehole is created as the sampling device is advanced downward. The Macro-Core Sampler collects samples continuously and requires that an open borehole be maintained for efficient sample recovery.

When the soil sampling device is retrieved from the borehole, the drive head, cutting shoe and/or piston assembly is removed, and the liner insert with sample is removed from the sampling device. The project geologist/sampling engineer is then given access to the sample for whatever purpose is required.

Table 1 summarizes the construction characteristics and sampling attributes for the Macro-Core Sampler.

7.2 Equipment Decontamination

Equipment decontamination procedures are specified within the project-specific work plan as well as in the ENSR SOP 7600Pines – Decontamination of Field Equipment.

7.3 Sampling Procedures - Macro-Core Sampler

(Note: These procedures are excerpted from Geoprobe™ Systems literature (1993). This SOP assumes that the subcontractor will perform sampling; therefore, detailed procedures regarding sample acquisition are not provided.)

7.3.1 Sampler Preparation

- Decontaminate the sampler parts (cutting shoe, sample tube) before assembly.
- Assemble the sampler by first placing the liner over the inside end of the cutting shoe, then inserting the liner/shoe assembly into the sample tube, and then finally threading the cutting shoe into the sample tube. Tighten the cutting shoe with the shoe wrench.
- Thread the sampler onto the drive head.

7.3.2 Sampling

- Using the percussion/probing machine, drive the sampler into the ground until the drive head reaches the ground surface.
- For deeper samples, the borehole walls must remain stable. The cutting shoe is designed with a tapered surface to limit sidewall scraping. Add additional probe rods until the sampler reaches the targeted sample interval, and then drive the sampler through the desired sample interval.
- Use the machine hydraulics to pull the sampler from the borehole.

7.3.3 Sample Recovery

- Once the sampler has been removed from the borehole, the sampler must be unthreaded from the drive head, the cutting shoe unthreaded from the sampler, and the liner/shoe assembly removed from the sample tube.
- Disconnect the cutting shoe from the liner which contains the soil sample. The recovered soil sample may now be viewed, logged, and extracted from the liner for analysis.

7.4 Sample Containment

7.4.1 General

- The soil sample can be removed from the liner following viewing and/or logging. Non-segmented Teflon® liners should be cut with a utility knife into approximate 6-inch lengths to facilitate sample extraction or to isolate specific sample zones targeted for analysis.

- Once the liner has been separated, the soil sample may be extracted from the individual liner segments with a spoon or spatula. The soil sample should be placed into a Teflon® sample collection pan and homogenized.

- The appropriate sample containers should be filled with soil from the collection bowl. A clean Teflon® spoon or spatula may be needed to fill the sample bottles as necessary. Use of fingers/hands to fill or pack sample containers is not allowed.

- All sampling equipment that is to be re-used should be decontaminated prior to reuse and investigation-derived waste (IDW) should be properly contained before leaving the area (see ENSR SOP No. 7600Pines – Decontamination of Field Equipment).

- The sample hole should be backfilled to eliminate any surface hazard. The project-specific work plan may indicate the requirements for backfilling of the sample hole.

7.5 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.
- Cap and label the container with the sample identifier, sampling date and time, preservation information, and analytical tests.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per SOP 1007Pines.
- Package the samples for shipment to the laboratory per SOP 7510Pines.

8.0 DATA AND RECORDS MANAGEMENT

Various forms are required to ensure that adequate documentation is made of the sample collection activities. These forms may include:

- Boring logs
- Field log books
- Sample collection records
- Chain-of-custody forms
- Shipping labels

Boring logs (Figure 2) will provide visual and descriptive information for samples collected at each soil boring and are often the most critical form of documentation generated during a soil sampling program. The field log book is kept as a general log of activities and should not be used in place of the boring log. Occasionally, sample collection records are used to supplement boring logs, especially for environmental samples which have been collected for laboratory analysis. Chain-of-custody forms are transmitted with the samples to the laboratory for sample tracking purposes. Shipping labels are required if sample coolers are to be transported to the laboratory by a third party (courier service). Original copies of these records should be maintained in the appropriate project files.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Collection of representative samples will be ensured through adherence to the procedures in this SOP and the sampling strategy outlined in the project-specific work plan. The field quality control samples identified in the project-specific work plan must be collected. These samples may include field duplicates, equipment rinsate blanks, and matrix spike/matrix spike duplicates (MS/MSDs).

10.0 REFERENCES

SOP 1007Pines – Chain-of-Custody Procedures. Revision 2.0.

SOP 7510Pines – Packaging and Shipment of Environmental Samples. Revision 2.0.

SOP 7600Pines – Decontamination of Field Equipment. Revision 1.0.

Geoprobe™ Systems, August 1993, “1993-94 Equipment and Tools Catalog”.

TABLE 1 - Geoprobe™ System Soil Sampler Characteristics

Sampler Type	Length (in.)	Diameter (in.)	Volume (ml)	Sleeve Liner Type	Suitability[1]			
					Soil Logging	Physical Testing	Chemical-Inorganics	Chemical-Organics
Macro-Core	45	1.5	1,300	Acetate Stainless Steel Teflon	A B A	A A A	A B A	B A A

[1] A - Preferred suitability
B - Acceptable suitability

FIGURE 1 Soil Sampling Tools – Macro-Core Sampler - Parts

SOIL SAMPLING TOOLS - Macro-Core Sampler - Parts

Macro-Core Sampler

AT-720 Series

The sampler features a nickel-plated sample tube that is 48" long x 2.0" in diameter, a hardened tool steel cutting shoe that has a 1.5" diameter opening, and a tapered drive head that fits standard Geoprobe probe rods. The overall length assembled is 51.25". Sample recovery is 45" long x 1.50" diameter (1302 ml) in a PETG liner.

PARTS

AT-720	MC Cutting Shoe
AT-721	MC Drive Head
AT-722	MC Sample Tube
AT-725	MC PETG (clear plastic) Liner
AT-726	MC Vinyl End Cap
AT-727	MC Shoe Wrench

KITS

Assembled Macro-Core Sampler*
Part No. AT-720K
Includes the following parts:
(1) **AT-720** MC Cutting Shoe
(1) **AT-721** MC Drive Head
(1) **AT-722** MC Sample Tube
*kit does not include liners and end caps

LINERS

AT-725K	MC PETG Liners (pre-flared, clear plastic) Box of 66 only
AT-726K	MC Vinyl End Caps (fit AT-725 liners) Box of 66 pairs (66 red/66 black)

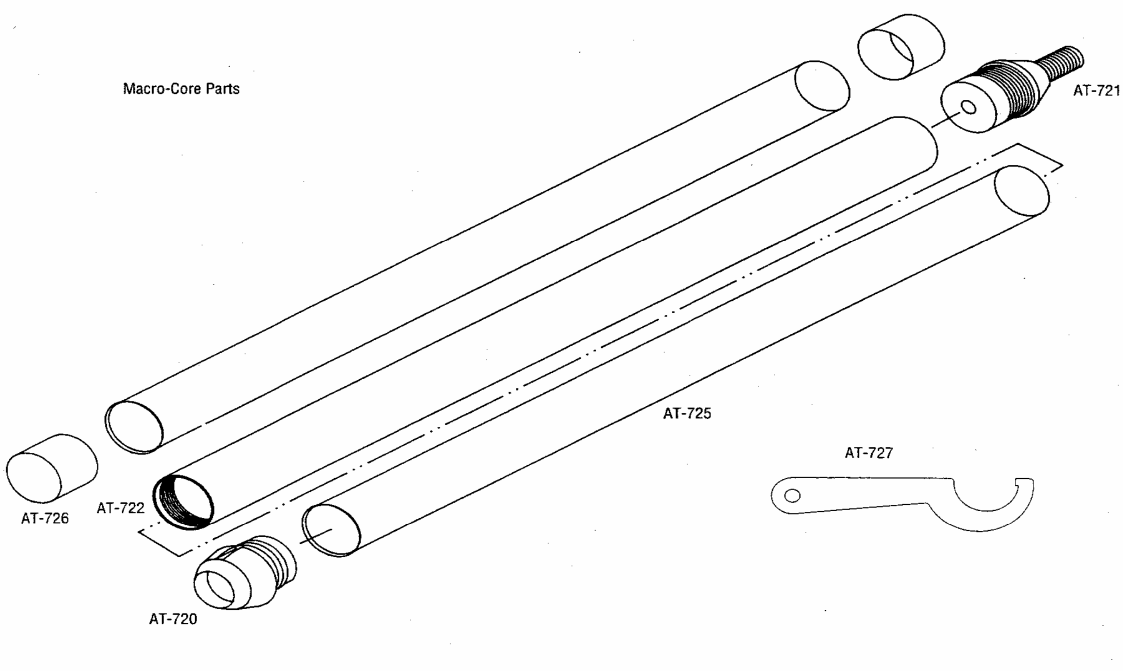


FIGURE 2 Boring Log

Project: Town of Pines
Boring / Well No.:
Description of Location:
Project No.: 01776-020
GPS:
Date:

ENSR Corporation
27755 Diehl Road
Warrenville, IL 60555

Elevation (ft)	Depth (ft)	U.S.C.S.	Sample Recovery (inches)	Density (SPT)	Lithologic Description	Well Construction	Remarks (Sample time, sample depth, etc.)
0	0				Ground Surface		
-1	1						
-2	2						
-3	3						
-4	4						
-5	5						
-6	6						
-7	7						
-8	8						
-9	9						
-10	10						
-11	11						
-12	12						
-13	13						
-14	14						

Drilling Contractor:
Drilling Method:
Staff / Geologist:
Sampling Method:

Sheet: 1 of 1

Groundwater Sample Collection from Monitoring Wells

SOP Number 7130Pines

Revision Number: 2.0

May 2005

ENSR Project Manager
May 23, 2005

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

Groundwater Sample Collection From Monitoring Wells

CONTENTS

LIST OF ACRONYMS

DO	Dissolved Oxygen
FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDEM	Indiana Department of Environmental Management
L/min	Liter per minute
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NTU	Nephelometric Turbidity Units
OLQ	Office of Land Quality
ORP	Oxygen Reduction Potential
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedure
TOC	Top of Casing
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operation Procedure (SOP) describes the method for collecting valid and representative samples of groundwater from monitoring wells. This SOP is written such that consideration of different sampling equipment may be used in different instances for collecting representative groundwater samples.

2.0 SUMMARY OF METHOD

Groundwater sample collection generally involves purging the stagnant water from a well while monitoring field parameters. After field parameters have stabilized, groundwater samples are then collected into the appropriate bottleware.

3.0 HEALTH AND SAFETY WARNINGS

Groundwater sampling may involve chemical hazards associated with exposure to materials in the groundwater being investigated and physical hazards associated with groundwater sampling equipment. When groundwater sampling is performed, adequate health and safety measures must be taken to protect field personnel. These measures will be addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between samples and sample locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

5.0 PERSONNEL QUALIFICATIONS

Groundwater sample collection is a relatively involved procedure requiring formal training and a variety of equipment. It is recommended that initial sampling of groundwater wells be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field sampling personnel to be familiar with the sampling procedures outlined within this SOP, and with specific sampling, quality assurance, and health and safety requirements outlined in the Field Sampling Plan (FSP), Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for collecting groundwater samples, decontamination of equipment, as well as proper documentation of sampling activities in the field logbook or field forms (as appropriate).

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Purging and Sampling Pumps
    - Peristaltic pumps
    - Grundfos Redi-flo2™ submersible pumps
    - Bladder pumps (if necessary)
- Field Instruments
    - Individual or multi-parameter meter(s) to measure temperature, pH, specific conductance, dissolved oxygen (DO), oxidation reduction potential (ORP), and/or turbidity
    - Water level meter
- Sample Collection Records (Figure 1)
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice)
- Filtration equipment (if necessary)
- Sample Chain-of-Custody forms (as required by ENSR SOP No. 1007Pines – Chain-of-Custody Procedures)
- Sample packaging and shipping supplies (as required by ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples)
- Waterproof marker or paint
- Distilled/deionized water supply
- Deionized water dispenser bottler
- Flow measurement cup or bucket
- Buckets

- Instrument calibration solutions
- Power source (generator or 12-volt marine battery)
- Paper towels
- Plastic sheeting
- Trash bags
- Zipper-lock bags
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 Instrument Calibration

Field instruments will be calibrated daily according to the requirements of the QAPP and manufacturer's specifications for each piece of equipment (e.g., ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor). Equipment will also be checked daily with the calibration solutions at the end of use of the equipment. Calibration records shall be recorded in the field logbook or appropriate field form.

7.2 Well Security and Condition

At each monitoring well location, observe the conditions of the well and surrounding area. The following information may be noted on the Groundwater Sample Collection Record (Figure 1) or in the field logbook:

- Condition of the well's identification marker
- Condition of the well lock and associated locking cap
- Integrity of the well - protective outer casing, obstructions or kinks in the well casing presence of water in the annular space, and the top of the interior casing
- Condition of the general area surrounding the well

7.3 Measuring Point Determination

Before collecting a water level measurement, check for an existing measuring point (notch, or other visible mark) established either at the time of well installation or by the latest survey. Generally, the measuring point is referenced from the top of the well casing (TOC), not the protective casing. If no measuring point exists, a measuring point should be established, clearly marked, and identified on the Groundwater Sample Collection Record (Figure 1) or the field logbook. The same measuring point should be used for subsequent sampling events.

7.4 Water Level Measurement

Water level measurements should be collected in accordance with ENSR SOP No. 101Pines – Water Level Measurements. The water level measurement should be entered on the Groundwater Sample Collection Record (Figure 1) or in the field logbook.

7.5 Purge Volume Calculation

Wells designated for sampling require purging to remove stagnant water in the well. A single casing volume of groundwater will be calculated after measuring the length of the water column and checking the well casing diameter. The Groundwater Sample Collection Record (Figure 1) provides information used to compute the casing volume, which includes a diagram, a numerical conversion table, and the standard calculation. The volume of standing water in the well (i.e., one purge volume) should be entered on the Groundwater Sample Collection Record (Figure 1).

7.6 Well Purging Methods and Procedures

7.6.1 Objectives

Prior to sample collection, purging must be performed for all groundwater monitoring wells to remove stagnant water from within the casing and gravel pack and to ensure that a representative groundwater sample is obtained.

All groundwater samples will be collected using low stress (low-flow) purging and sampling procedures according to the United States Environmental Protection Agency (USEPA) Region 1 SOP titled “Low Stress Purging and Sampling

Procedure for the Collection of Groundwater Samples from Monitoring Wells", Revision 2, July 1996 (USEPA, 1996) and Indiana Department of Environmental Management (IDEM) Office of Land Quality (OLQ) Geological Services Technical Memorandum titled "Micro-Purge Sampling for Monitoring Wells" dated January 8, 2003 (IDEM, 2003). The low-flow method emphasizes the need to minimize water level drawdown and low groundwater pumping rates to collect samples with minimal alterations to groundwater chemistry.

During well purging, the water level will be measured with a water level meter in accordance with ENSR SOP No. 101Pines – Water Level Measurement. Water level drawdown and flow rate will be recorded on the Groundwater Collection Record (Figure 1). A final purging rate will be selected that does not exceed 0.5 liters per minute (L/min) (typically between 0.1 L/min and 0.3 L/min), and results in a stable drawdown, ideally less than 0.3 feet.

The general types of non-dedicated equipment used for well purging include surface pumps and down-well pumps. The purge method and equipment selected is specified in the FSP. For this project, peristaltic pumps will be used where depths to water are sufficiently shallow, and submersible pumps used where depths to water are too great for peristaltic pumps.

Purge water will be pumped through a flow-through cell and the following parameters will be measured: pH, specific conductivity, temperature, DO, and ORP. These parameters will be measured with a water quality meter, calibrated according to the manufacturer's specifications (see ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor). Turbidity will be measured separately with a nephelometer, also calibrated to the manufacturer's specifications (see ENSR SOP No. 108Pines – Field Measurement of Turbidity). A round of parameter measurements will be recorded after the flow-through cell is full, approximately 10 minutes after the flow-through cell is full, and then approximately every 5 minutes thereafter, until parameter values have stabilized.

Purging is considered complete and sampling may begin when all parameter values have stabilized and turbidity is below 5 Nephelometric Turbidity Units (NTU). Stabilization is considered to be achieved when three consecutive readings, taken at 3- to 5-minute intervals, are within the following limits:

- Turbidity : less than 5 NTU or ± 10%
- DO : ± 10%
- Specific Conductance : ± 3%
- Temperature : ± 3%
- pH : ± 0.1 standard units
- ORP : ± 10 millivolts

Every effort will be made to lower the turbidity to less than 5 NTU before sampling. If the turbidity cannot be reduced to below 5 NTU, the pumping rate should be reduced. If turbidity still cannot be reduced below 5 NTU, samples may be collected if all other parameters are stable and the turbidity is stable, that is, not improving. The condition will be noted on the field form or in the logbook.

If low-flow purging cannot be achieved for a particular well (typically due to insufficient yield to establish a stable drawdown), the well may be purged dry, then sampled when sufficient water has recharged. The condition will be noted on the field form or in the logbook.

7.6.2 Surface Pumps

General

Well purging using pumps located at the ground surface can be performed with a peristaltic pump if the water level in the well is within approximately 20 feet of the top of the well.

Peristaltic pumps provide a low rate of flow typically in the range of 0.02-0.2 gallons/minute (gal/min) (0.075-0.750 L/min). Peristaltic pumps are suitable for purging situations where disturbance of the water column must be kept minimal for particularly sensitive analyses and where volatile organic compounds are not being analyzed.

Peristaltic Pump Procedure

Attach a new suction and discharge line to the peristaltic pump. Silicon tubing must be used through the pump head and must meet the pump head specifications. A second type of tubing (e.g., polyethylene) may be attached to the silicon tubing for use as the suction and discharge lines. The suction line must be long enough to extend to the static groundwater surface and reach further should drawdown occur during pumping.

Measure the length of the suction line and lower it down the monitoring well until the end is located at the midpoint of the saturated screen and at least 2 feet above the bottom of the well to preclude excess turbidity from the bottom of the well. Start the pump and direct the discharge into a graduated bucket. Adjust the pumping rate with the speed control knob so that a smooth flowing discharge is attained.

Measure the pumping rate by recording the time required to fill a flow measurement cup or bucket. The pumping shall be monitored to assure continuous discharge. If drawdown causes the discharge to stop, the suction line will be lowered very slowly further down into the well until pumping restarts. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet.

7.6.3 Down-Well Pumps

General

Groundwater withdrawal using non-dedicated down-well pumps may be performed with a submersible pump or a bladder pump.

Electric submersible pumps provide an effective means for well purging and in some cases sample collection. Submersible pumps are particularly useful for situations where the depth to water table is greater than 20 feet and where the depth or diameter of the well requires that a large purge volume be removed before sample collection.

A commonly available submersible pump, the Grundfos Redi-Flo2™ pump, is suited for operation in 2-inch or larger internal diameter wells. Pumping rates are adjusted to low-flow levels by adjusting the current to the pump motor rather than using a flow valve.

As an alternative method to using the submersible pump, bladder pumps may also be used. Bladder Pumps usually consist of a stainless steel pump housing with an internal Teflon® or polyethylene bladder. Discharge and air line tubing is connected to the bladder pump to the air compressor and control unit. The pump is operated by lowering it into the water column within the well screen, then pulsing air into the bladder from the air compressor and pump controller unit. Pumps and controllers are often not interchangeable between manufacturers; therefore, it is usually necessary to have both items provided by the same manufacturer. Pump bladders are generally field-serviceable and replaceable.

A check of well condition may be required prior to inserting any down-well pump if the well has not been sampled for some time or if groundwater quality conditions are not known. The well condition check should include a check of casing plumbness as a bent well casing could cause a pump to get stuck. Casing plumbness can be checked by lowering a clean cylindrical tube with the approximate pump dimensions into the well. If the well casing is not plumb then an alternative purging method should be used.

Submersible pumps (i.e., Grundfos Redi-Flo2™) will generally be used in wells where water levels are too deep to allow use of a peristaltic pump.

Electric Submersible Pump Procedure

Slowly lower the submersible pump with attached discharge line into the monitoring well taking notice of any roughness or restriction within the well riser pipe. The pump should be placed in the uppermost section of the static water column of the monitoring well. The power cord should be attached to the discharge line with an inert material (i.e., zip-ties) to prevent the power cord from getting stuck between the pump, discharge line, and the well casing. Secure the discharge line and power cord to the well casing, using tape or a clamp, taking care not to crimp or cut either the discharge line or power cord.

Connect the power cord to the power source (i.e., rechargeable battery pack, auto battery, or generator) and turn the pump on. Voltage and amperage meter readings on the pump controller (if provided) should be monitored closely during purging. The operations manual for the specific pump used should be reviewed regarding changes in voltage/amperage and the potential impacts on pump integrity. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet. Pumping should be discontinued if warning conditions occur and/or if the well is pumped to where drawdown falls below the pump's intake level.

<u>Bladder Pump Procedure</u>

As an alternative method to the submersible pump, bladder pumps may be used. To operate the bladder pump system, the pump and discharge line should be lowered into the well close to the bottom of the well screen, then secured to the well casing with a clamp. The air compressor should then be turned on to activate pumping. The pump controller is used to vary the discharge rate to the required flow. The pumping rate will be adjusted so that drawdown is stabilized, ideally at a level less than 0.3 feet.

7.7 Sample Collection Methods and Procedures

7.7.1 Objectives

Groundwater samples can be collected using similar methods employed for purging. In most cases during sampling, groundwater will be transferred to the appropriate containers directly from the discharge source. It is important that the tubing from the pump to the flow-through cell be disconnected prior to sample collection. During transfer, discharge tubing and other equipment shall not contact the inside of the sample containers.

Groundwater samples that may require filtration (e.g., due to elevated turbidity), will be filtered in accordance with ENSR SOP No. 7131Pines – Field Filtration of Water Samples for Inorganic Constituents.

7.7.2 Surface Pumps

The methods and procedures described in Section 7.7.2 for peristaltic pumps also apply to groundwater sample collection.

Sample bottles shall be filled directly from the pump's discharge line (after tubing has been disconnected from the flow-through cell) and care shall be taken to keep the discharge tube from contacting the sample container.

7.7.3 Down-Well Pumps

Using the pump methods described in Section 7.6.3, groundwater samples can be collected from either the electric submersible or bladder pump directly from the discharge line (after tubing has been disconnected from the flow-through cell). Sample bottles will be filled directly from the discharge line of the pump.

7.8 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.
- Cap and label the container with (at a minimum) the sample identifier and sampling date and time. Additional information such as preservation information and analytical tests may also be added to the sample label as appropriate.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.
- Package the samples for shipment to the laboratory per ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

7.9 Equipment Decontamination

All equipment that comes into contact with groundwater (e.g., submersible pumps) should be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Equipment protocol before moving to the next location. Dedicated or disposable equipment does not need to be decontaminated.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding sample collection should be documented in several areas: the sample chain-of-custody record, sample collection record, field logbook, and sample labels or tags. Additional information regarding each form of documentation is presented in the following paragraphs:

8.1 Sample Chain-of-Custody Record

This standard form requires input of specific information regarding each collected sample for laboratory analytical purposes, as specified in ENSR SOP No. 1007Pines – Chain-of-Custody Procedures and ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

8.2 Sample Collection Record

This form (Figure 1) requires input of specific information regarding the collection of each individual sample including sample identification, water quality parameters, collection method, and containers/preservation requirements.

8.3 Field Logbook

This logbook should be dedicated to the project and should be used by field personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process.

8.4 Sample Labels

Sample labels shall be completed at the time each sample is collected and attached to each sample container. Sample labeling will be conducted per the FSP and QAPP. Labels may include the information listed below.

- Project number (not project name)
- Sample number
- Sample designation
- Analysis type
- Preservative
- Sample collection date
- Sample collection time
- Sampler's name

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as field duplicate, equipment and/or field blanks and matrix spike/matrix spike duplicate (MS/MSD) samples. These requirements are outlined in the FSP and QAPP. Additional information regarding quality assurance sample collection relevant to groundwater sampling is described below.

9.1 Field Blank/Equipment Blank Sample Collection

Field blank samples serve as a quality assurance check of equipment and field conditions at the time of sampling. Field blank samples are usually prepared by transferring analyte-free water into a clean set of sample containers, then analyzing it as a sample. Sometimes, the analyte-free water is transferred over or through the sampling device before it is placed into the sample containers. This type of field blank sample is known as an equipment blank. The FSP and QAPP contains specific information regarding the type and number of field blanks or equipment blanks required for collection.

9.2 Field Duplicate Sample Collection

Field duplicate samples are collected for the purpose of providing two sets of results for comparison. To the extent possible based on available information, field duplicates will be selected at locations with the likelihood of detectable concentrations of constituents. These samples are used to assess precision. Duplicate samples are usually prepared by splitting the sample into two sets of sample containers, then analyzing each set as a separate sample. The QAPP contains specific information regarding the type and number of duplicate samples for collection.

9.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample Collection

MS/MSDs provide information about the effect of the sample matrix on digestion and measurement methodology. For samples submitted for MS/MSD analysis, triple sample volume is generally required. The QAPP contains specific information regarding the frequency of MS/MSD samples.

10.0 REFERENCES

Code of Federal Regulations, Chapter 40 (Section 261.4(d)).

ENSR SOP No. 105Pines - Operation and Calibration of the YSI Multi-Parameter Water Quality Monitor.

ENSR SOP No. 101Pines – Water Level Measurements.

ENSR SOP No. 108Pines – Field Measurement of Turbidity.

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

ENSR SOP No. 7131Pines – Field Filtration of Water Samples for Inorganic Constituents.

ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0

IDEM. 2003. OLQ Geologic Services Technical Memorandum – Micro-Purge Sampling for Monitoring Wells. Indiana Department of Environmental Management Office of Land Quality. January 8, 2003.

USEPA. 1996. Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples From Monitoring Wells, Revision 2. U.S. Environmental Protection Agency, Region 1. July 30, 1996.

FIGURE 1 – EXAMPLE GROUNDWATER SAMPLE COLLECTION RECORD

ENSR

Well ID:

Low Flow Ground Water Sample Collection Record

Client: ______________________ Date: __________ Time: Start ________ am/pm
Project No: ______________________ Finish ________ am/pm
Site Location: ______________________
Weather Conds: ______________________ Collector(s): ______________________

1. WATER LEVEL DATA: (measured from Top of Casing)

a. Total Well Length ________ c. Length of Water Column ________ (a-b) Casing Diameter/Material ________

b. Water Table Depth ________ d. Calculated System Volume (see back) ________

2. WELL PURGE DATA

a. Purge Method: ______________________

b. Acceptance Criteria defined (see workplan)

- Temperature	3%	-D.O.	10%
- pH	± 1.0 unit	- ORP	± 10mV
- Sp. Cond.	3%	- Drawdown	< 0.3'

c. Field Testing Equipment used: Make Model Serial Number

Time (24hr)	Volume Removed (Liters)	Temp. (°C)	pH	Spec. Cond. (µS/cm)	DO (mg/L)	ORP (mV)	Turbidity (NTU)	Flow Rate (ml/min)	Drawdown (feet)	Color/Odor

d. Acceptance criteria pass/fail Yes No N/A

(continued on back)

Has required volume been removed ☐ ☐ ☐
Has required turbidity been reached ☐ ☐ ☐
Have parameters stabilized ☐ ☐ ☐
If no or N/A - Explain below.

____

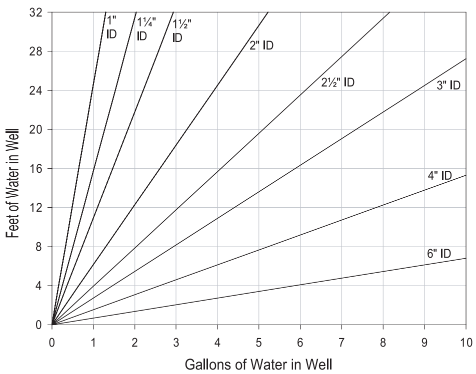
3. SAMPLE COLLECTION: Method: ______________________

Sample ID	Container Type	No. of Containers	Preservation	Analysis Req.	Time

Comments ______________________

Signature ______________________ Date ________

Purge Volume Calculation



Volume / Linear Ft. of Pipe		
ID (in)	Gallon	Liter
0.25	0.0025	0.0097
0.375	0.0057	0.0217
0.5	0.0102	0.0386
0.75	0.0229	0.0869
1	0.0408	0.1544
1.25	0.0637	0.2413
1.5	0.0918	0.3475
2	0.1632	0.6178
2.5	0.2550	0.9653
3	0.3672	1.3900
4	0.6528	2.4711
6	1.4688	5.5600

(continued from front)

Time (24 hr)	Volume Removed (Liters)	Temp (°C)	pH	Spec. Cond. (µS/cm)	DO (mg/L)	ORP (mV)	Turbidity (NTU)	Flow Rate (ml/min)	Drawdown (ft)	Color/Odor

Field Filtration of Water Samples for Inorganic Constituents

SOP Number 7131Pines

Revision Number: 1.0

May 2005

ENSR Project Manager
May 23, 2005

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

CONTENTS

APPENDICES

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
QC	Quality Control
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) is concerned with the field filtration of water samples for inorganic analyses. The specific analyses that require filtration will be defined in each project-specific work plan. The most common parameters requiring filtration, however, are dissolved metals and orthophosphate.

2.0 SUMMARY OF METHOD

Field filtration of water samples typically involves passing water from a sampling point through a filtration system to remove solids and other large diameter impurities. Generally, a pump and in-line disposable filter cartridge is used to filter the sample. Filtering can be accomplished directly from the sampling point or via some type of intermediate storage container. The resulting filtrate is discharged into approved sample containers, preserved (if required by the method), and submitted for analysis.

Prior to the advent of disposable filter cartridges, sample filtration was often accomplished using a tripod filter stand containing replaceable filter membranes that were under pressure. Use of the tripod filter stand was generally time consuming because it required decontamination after each use, frequent filter membrane changes, and use of compressed nitrogen gas. This SOP no longer promotes use of this system although it may still be considered suitable for use as a backup system should filter cartridges be unavailable.

If a pump is being used to collect the sample, for example, from a monitoring well, that pump should also be used for filtration. That is, the in-line disposable filter cartridge should be placed along the pump discharge hose. Where this is not possible or if a pump is not being used for sample collection, it is recommended that a peristaltic pump be used to pass the water through the filter. The peristaltic is the pump of choice over other pumping systems for filtering because back pressure caused by gradual filter clogging will not affect the pump's integrity.

3.0 HEALTH AND SAFETY WARNINGS

Sample filtration may involve chemical hazards associated with exposure to materials in the water being investigated. When conducting field filtering, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

The presence of suspended sediment or particulates in water samples may lead to bias in the analysis and interpretation of the results. Filtering is used to remove these particles from the sample prior to analysis. However, filtering will only remove those particles larger than the size of the filter. This should be considered in evaluating data from filtered samples, as appropriate.

Once samples are collected (i.e., removed from their native environment), chemical changes occur. This is particularly true for groundwater samples, where the subsurface is not in equilibrium with atmospheric conditions. These chemical changes can result in precipitation of metals from solution, which will change both the chemistry of the water and the nature of the suspended particulates. Therefore, filtering will be conducted as soon as feasible once a sample is collected.

New filters will be used for each sample that is to be filtered to avoid the potential for cross-contamination.

5.0 PERSONNEL QUALIFICATIONS

Sample filtration is a relatively simple procedure requiring minimal training and a minimal amount of equipment. It is recommended that initial attempts be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP and Field Sampling Plan (FSP), and quality assurance and health and safety requirements outlined within the Quality Assurance Project Plan (QAPP) and HASP. Field personnel are responsible for field filtration being conducted in a manner consistent with this SOP, that proper decontamination procedures are followed, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Peristaltic pump (or other pump) with 12v power supply (if necessary)
- Silicone pump tubing (for peristaltic pumps - approximately 2 feet per sample)
- Polyethylene, or other type of influent/discharge tubing (optional)
- Disposable 0.45-micron filter cartridges (high-capacity and/or low-capacity)
- Small hose clamps/screwdriver
- Intermediate sample containers
- Sample kit (i.e., bottles, labels, preservatives, custody records and tape, cooler, ice), if needed
- Sample Chain-of-Custody forms (as required by ENSR SOP No. 1007Pines – Chain-of-Custody Procedures)
- Sample packaging and shipping supplies (as required by ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples)
- Health and safety supplies (as required by the HASP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Sample Collection Records
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

Sample filtration should be conducted in as clean an environment as possible but can be accomplished almost anywhere including at the sampling point, the field vehicle, and/or at a remote or centralized sample handling area (i.e., the field trailer). The sample should be filtered as soon as possible after sample collection, before the sample chemistry changes, and prior to sample preservation (if required).

Prior to start of sample filtration, if the sampling pump is not being used, field personnel will set the equipment up and check that everything is operational. Set-up includes establishing the filtering location, hooking up the peristaltic pump to a power supply (if no internal battery supply is available), feeding a short length of pump tubing through the pump head, and attaching a filter cartridge with discharge arrow pointing in the direction of sample discharge. Additional information on pump set-up appears in the following section.

7.2 Pump Set-up (if applicable)

7.2.1 Place the pump on a stable surface and connect it to the available power supply (if required). Turn the pump on and vary the speed control knob to check that the pump is operational. The roller assembly should visibly change its rate of rotation as the speed control knob is turned. Keep the speed control knob set fairly low to install pump tubing. Switch the pump off.

7.2.2 Cut an approximate 2-foot length of clean silicone pump head tubing from the tubing roll. Loosen the 3 adjusting screws on the pump head assembly and pull the front cover forward to make it easier to feed the pump tubing. The cover/screws do not need to be removed completely.

7.2.3 Insert one end of the pump tubing into the pump head assembly until it contacts the first roller. Switch the pump on so that the rollers turn in the direction that the tubing is being fed. The tubing should feed through the pump head assembly by itself; however, pushing on it slightly will help. Shut off the pump when the tubing is threaded through a sufficient length to allow the influent end to reach the intermediate sample container and the discharge end to reach the final sample bottle.

7.2.4 Tighten the screws on the pump head assembly.

7.3 Filtration Procedure

7.3.1 Filtration from Intermediate Containers

- Obtain a representative water sample following standard sample collection procedures and place it into an intermediate sample container. This container should be of similar type and size as the final sample container. Depending on the final sample volume that is required, it may be necessary to collect excess sample volume for filtering. The container should be unpreserved. Cap the container and bring it to the sample filtration area.

- Select a new low-capacity or high-capacity filter cartridge based on the sample turbidity (if the sample is nearly clear, a low-capacity filter may suffice). Remove the filter from its wrapper and attach it to the discharge end of the pump tubing. Make sure that the filter flow direction, usually indicated by an arrow, points in the intended flow direction.

- Obtain a new sample bottle and place it on a stable platform. Check the tubing lengths on either side of the pump head assembly at this time and adjust them as necessary by loosening the pump head assembly screws and pulling on the tubing.

- Remove the cap from both containers then insert the influent end of the pump head tubing (i.e., intake line) into the intermediate sample container so that it is at least one-third of the way into the container. Pumping from the upper third of the intermediate container, then gradually lowering the intake line into the container, will help extend the life of the filter.

- Start the pump with the speed control knob set to a fairly low speed and observe the rate of flow through the tubing. Allow 50 to 100 milliliters of water to pass through the filter into a waste container. This will flush any residual water from the manufacturing process through the filter.

- Transfer the discharge end of the filter cartridge to the top of the final sample container. As filtration proceeds, gradually lower the intake line until the sample has been filtered. Replace the filter if necessary at any time during the filtration procedure (see Section 7.4). Fill the final container to the desired level.

7.3.2 Surface Water Sample Filtration

If surface water sample collection and filtration is performed using a peristaltic pump, the apparatus and procedures are the same as for other samples. The only significant difference is that when collecting a surface water sample in this manner, field personnel must be sure that the pump intake line is positioned at the desired location and depth within the surface water body. It may be necessary to collect subsurface water samples at specific depths in this manner; however, it may be easier to collect surface water samples into intermediate sample containers than to obtain a filtered sample directly from the surface water body. Collection of surface water samples is detailed in ENSR SOP No. 103Pines – Surface Water and Sediment Sample Collection.

7.3.3 Filtration of Samples from Wells

If a submersible pump is being used for sample collection, the in-line filter cartridge can be attached to the pump discharge line or an alternate method may be used to collect the sample using intermediate sample containers. The peristaltic pump has a suction limit of approximately 20 feet. If the water level in the well is below that limit, a peristaltic pump cannot be used to collect samples. Collection of surface water samples is detailed in ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells.

7.4 Filter Replacement

High sample turbidity may cause clogging of the filter membranes, a decrease in filtration efficiency/rate, and occasionally, such a high pressure that the filter cartridge is prematurely released from the pump head tubing. If the rate of flow is observed to decrease substantially, then it is recommended that the filter be replaced. In order to do this safely, the following steps should be followed.

7.4.1 Remove the discharge end of the tubing from the sample container. Turn the pump off, and then reverse the pump head rotation direction by using the forward/reverse switch. Turn the pump back on to release backpressure from the filter and tubing. Turn the pump off again and remove the old filter.

7.4.2 Obtain a new filter and install it as indicated in Section 7.3 including pumping 50 to 100 milliliters of sample water through the filter into a waste container. Resume filtering.

7.5 Sample Handling and Preservation

- Once each sample container is filled, clean the rim and threads of the sample container by wiping with a paper towel.
- Cap and label the container with (at a minimum) the sample identifier and sampling date and time. Additional information such as preservation information and analytical tests may also be added to the sample label as appropriate.
- Place the sample containers into a cooler and maintain on ice.
- Complete sample chain-of-custody and other documentation per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

- Package the samples for shipment to the laboratory per ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding filtered water sample collection will be documented on the sample collection record and the field project logbook.

8.1 Sample Collection Record

This form requires input of specific information regarding the collection of each individual sample including sample identification, sample type, collection method, containers, parameters to be analyzed, sample preservation method, sample collection time, time of sample filtration, and type, size and number of filters used. Any deviations from the approved work plan or this SOP must be documented on the sample collection record or in the field logbook.

8.2 Field Logbook

The logbook will be dedicated to the project and will be used by sampling personnel to maintain a general log of activities throughout the sampling program. This logbook should be used in support of, and in combination with, the sample collection record. Documentation within the logbook should be thorough and sufficiently detailed to present a concise, descriptive history of the sample collection process including specific information regarding the sample filtration equipment used.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP. Quality assurance requirements typically suggest the collection of a sufficient quantity of quality control (QC) samples such as equipment blanks and field duplicate samples. These requirements are outlined in the FSP and QAPP. Field duplicates must be filtered if their parent samples are also filtered.

10.0 REFERENCES

ENSR SOP No. 103Pines – Surface Water and Sediment Sample Collection.

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

ENSR SOP No. 7510Pines – Packaging and Shipment of Environmental Samples.

ENSR SOP No. 7130Pines – Groundwater Sample Collection from Monitoring Wells.

APPENDIX – GLOSSARY

Filter Cartridges – In-line 0.45-micron disposable filter cartridges are commercially available as a substitute to the former filter stand apparatus with replaceable filter membranes. The cartridges contain an inert filter membrane material sealed within a polyethylene case. The influent and effluent ports contain fittings for tubing attachment. Two types of cartridges are available, a low-capacity cartridge with 20 cm^2 of effective filtration area, and a high-capacity cartridge with 700 cm^2 of filtration area. Low-capacity cartridges are effective only with low to no-visible turbidity within the sample. High-capacity cartridges, which are more expensive, are suitable for a wide range of sample turbidity. Larger pore size filter cartridges are also commercially available. These should not be used unless specifically required in the sampling plan.

Influent/Discharge Tubing - Silicone pump tubing is generally too expensive to use for influent and/or discharge tubing if, for instance, pumping the sample directly from a well is required. Polyethylene tubing of a slightly narrower outside diameter than the silicone tubing may be used for influent/discharge tubing, if necessary. The two types of tubing can usually be joined without clamps as silicone tubing is very flexible and sticky.

Intermediate Sample Containers - Intermediate sample containers generally consist of a clean unpreserved sample container of equal or larger volume and type which is used to temporarily store the sample until it is filtered. The sample is usually filtered directly from the intermediate containers into the final sample container. Intermediate sample containers should be disposed of after each use. An adequate supply of sample containers should be available to meet project requirements.

Peristaltic Pump - This type of pump is a low volume pump which operates by progressively squeezing the water sample through a silicon tube by means of 3 rollers which revolve within a housing. The advantage of this type of pump is that the sample never contacts any mechanical parts of the pump.

Pump Tubing - The pump tubing is made of silicone with a specific inside and outside diameter that matches the pump head design. Be sure to check the pump head number against the tubing number. These numbers should be the same and are located on the pump roller housing and on the tubing package respectively. Use of the wrong tubing will either diminish the effectiveness of the pump or will cause it to stop operating entirely.

Monitoring Well Construction and Installation

SOP Number 7220Pines

Revision Number: 1.0

January 2005

ENSR Project Manager
January 18, 2005

ENSR Project QA Officer
January 18, 2005

ENSR Corporation
January 2005
Pines Area of Investigation

CONTENTS

APPENDICES

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDW	Investigation Derived Waste
OSHA	Occupational Safety and Health Administration
PVC	Poly Vinyl Chloride
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) provides guidance for installing groundwater monitoring wells. Monitoring wells may be installed to monitor the depth to groundwater, to measure aquifer properties, and to obtain samples of groundwater for chemical analysis.

This SOP is applicable to installation of single monitoring wells within a borehole. The construction and installation of nested, multilevel or other special well designs is not proposed in the Field Sampling Plan (FSP), nor are the methods covered within this SOP.

2.0 SUMMARY OF METHOD

Monitoring well construction and installation generally involves drilling a borehole using conventional drilling equipment, installing commercially available well construction and filter/sealing materials, and development of the well prior to sampling. This SOP covers well construction and installation methods only. Well development methods are covered under ENSR SOP No. 7221Pines - Monitoring Well Development.

3.0 HEALTH AND SAFETY WARNINGS

Monitoring well installation may involve chemical hazards associated with exposure to materials in the groundwater being investigated and physical hazards associated with drilling equipment and installation methods. When monitoring wells are installed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between borehole locations. Minimization of the cross-contamination will occur through the use of clean sampling tools at each location, which will require decontamination of sampling equipment as per ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

Other potential interferences may be due to the well materials, or to interactions between well materials and the formation. Because the constituents being monitored for this project are primarily metals and inorganics, well materials in contact with groundwater to be sampled will be constructed of plastics and not metals. The process of installing a well necessarily disturbs the geologic formation. Wells will be developed appropriately as described in ENSR SOP No. 7221Piness – Monitoring Well Development. The wells will be allowed to stabilize a minimum of two weeks after development before a well is sampled.

Cross-contamination may result when surface water runoff or other materials enter the well from the ground surface. To minimize this, wells will be installed with stick-up casings wherever possible. Where such wells may be at risk of damage from traffice (i.e., near roadways), bumpers may be placed around the well to prevent them from being hit. Where flush-mount well completions are necessary, appropriate steps will be taken to reduce the potential for infiltration into the well as described below.

5.0 PERSONNEL QUALIFICATIONS

Well construction and installation requires a moderate degree of training and experience as numerous drilling situations may occur that will require field decisions to be made. It is recommended that inexperienced personnel be supervised for several well installations before working on their own. Geologists or personnel with geologic experience should supervise well installation. The geologic work performed under this SOP will be conducted under the direction of a professional geologist licensed to practice in Indiana.

Field and subcontract personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of the field personnel to directly oversee the construction and installation of the monitoring well by the drilling subcontractor to ensure that the well installation specifications defined in the FSP are adhered to. It is also the responsibility of the field personnel to be familiar with the procedures outlined within this SOP, quality assurance, and the health and safety requirements outlined within the FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for monitoring wells being installed in a manner consistent with this SOP, that proper decontamination procedures are followed, as well as proper documentation in the field logbook or field forms (if appropriate).

It will be the responsibility of the drilling subcontractor to provide a trained operator and the necessary equipment for well construction and installation. Well construction materials should be consistent with project requirements as specified in the FSP.

It is the responsibility of the surveying subcontractor to provide one or more of the following well measurements as specified in the FSP: ground surface elevation, horizontal well coordinates, top of well casing elevation (i.e., top-of-casing, or measuring point elevation), and/or top of protective casing elevation.

6.0 EQUIPMENT AND SUPPLIES

6.1 Well Construction Materials

Well construction materials are usually provided by the drilling subcontractor. For this project, because the primary constituents to be analyzes are metals, the wells will consist of commercially available flush-threaded well screen and riser pipe constructed of poly vinyl chloride (PVC) with a minimum 2-inch inside diameter as specified in the FSP.

6.2 Well Completion Materials

Well completion materials include silica sand, bentonite, cement, protective casings, and locks. Completion materials are generally provided by the drilling subcontractor.

6.3 Other Required Materials

Other required materials include the following:

- Monitoring Well Construction Diagrams (Figure 1)
- Potable water supply
- Plastic sheeting
- Trash bags
- Paper towels
- Water level meter
- Waterproof marker or paint (to label wells)
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)

- Health and safety supplies (as required by the HASP)
- Appropriate containers and materials to manage investigation-derived waste (IDW) (as specified in the FSP)
- Approved plans (e.g., HASP, FSP, QAPP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

7.1.1 Borehole Preparation

Standard drilling methods should be used by the drilling subcontractor under the supervision of field personnel to achieve the desired drilling/well installation depths specified in the FSP.

The diameter of the borehole must be a minimum of 2 inches greater than the outside diameter of the well screen or riser pipe used to construct the well. This is necessary so that sufficient annular space is available to install filter packs, bentonite seals, and grout seals. For this project, 2-inch diameter PVC well materials will be installed inside 6-inch diameter augers as specified in the FSP.

7.1.2 Well Material Decontamination

New well materials (well screen and riser pipe) generally arrive at the site boxed and sealed within plastic bags, so decontamination prior to use is not anticipated. However, well materials should be inspected by the field personnel upon delivery to check cleanliness. If the well materials appear dirty, then they should be decontaminated prior to use. Well casing and riser may be decontaminated by steam-cleaning by the drilling subcontractor in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment. For smaller materials such as caps, they may be decontaminated using detergent and water in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

7.2 Well Construction Procedure

7.2.1 Depth Measurement

Once the target drilling depth has been reached, the drilling subcontractor will measure the total open depth of the borehole with a weighted tape measure. Adjustments of borehole depth can be made at this time by drilling further or installing a small amount of sand filter material to achieve the desired depth. The water table depth may also be checked with a water level indicator if this measurement cannot be obtained with the weighted tape.

7.2.2 Well Construction

The well screen and riser pipe generally are assembled by hand as they are lowered into the borehole through the hollow-stem augers. Before the well screen is inserted into the borehole, the full length of the slotted portion of the well screen as well as the unslotted portion of the bottom of the screen should be measured with a measuring tape. These measurements should be recorded on the well construction diagram.

After the above measurements have been taken, the drilling subcontractor may begin assembling the well. As the assembled well is lowered, care should be taken to ensure that it is centered in the hole. The well should be temporarily capped or covered before filter sand and other annular materials are installed. The well should be set at the base of the borehole, and this should be confirmed by observation or measurement at the time of installation.

7.2.3 Filter Sand Installation

The drilling subcontractor should fill the annular space surrounding the screened section of the monitoring well to at least 1 foot above the top of the screen with an appropriately graded, clean sand or fine gravel. In general, the filter pack should not extend more than 3 feet above the top of the screen to limit the thickness of the monitoring zone. If coarse filter materials are used, an additional 1-foot thick layer of fine sand should be placed immediately above the filter pack to prevent the infiltration of sealing components (bentonite or grout) into the filter pack. As the filter pack is placed, a weighted tape should be lowered into the annular space to verify the depth to the top of the layer. Depending upon depth, some time may be required for these materials to settle. If necessary, to eliminate possible bridging or creation of voids, placement of the sand pack may require the use of a tremie pipe. Tremie pipe sandpack installations are generally suggested for deep water table wells and for wells that are screened some distance beneath the water table. The augers should be gradually removed from around the well as the sand pack is being installed.

7.2.4 Bentonite Seal Installation

A minimum 2-foot thick layer of bentonite pellets or slurry seal will be installed by the drilling subcontractor immediately above the well screen filter pack in all monitoring wells. The purpose of the seal is to provide a barrier to vertical flow of water in the annular space between the borehole and the well casing. Bentonite is used because it swells significantly upon contact with water. Pellets or chips generally can be installed in shallow boreholes by pouring them very slowly from the surface. If they are poured too quickly, they may bridge at some shallow, undesired depth. As an option, powdered bentonite may be mixed with water into a thick slurry and a tremie pipe can be used to inject the material at the desired depth. The bentonite materials will be hydrated by adding water to them after they have been placed in the borehole.

7.2.5 Annular Grout Seal Installation

The remainder of the annular space between the bentonite seal and the ground surface will be filled with grout. This grout seal should consist of a bentonite/cement mix with a ratio of bentonite to cement of between 1:5 and 1:20. The grout ratio should be chosen by the drilling subcontractor based on site conditions with a higher percentage of bentonite generally used for formations with higher porosity. The grout material will be mixed with water and placed into the borehole using a tremie pipe.

The borehole annulus will be grouted with seal materials to within 3 feet of the ground surface. Drill cuttings will not be used as backfill material.

7.2.6 Well Completion

The drilling subcontractor will cut the top of the well to the desired height and install a locking cap. Well casings are usually cut to be a certain height above ground surface (typically 2.5 to 3 feet) or are cut to be flush with the ground surface, depending on the well location.

7.2.7 Protective Casing/Concrete Pad Installation

The drilling subcontractor will install a steel guard pipe on the well as a protective casing. A 2-foot by 2-foot cement apron will be installed to hold the protective casing (i.e., road boxes or stand up casing) in place. The surface of the concrete pad will be sloped so that drainage occurs away from the well. Flush-mount protective casings may not require an extensive concrete pad and should be completed such that they are slightly mounded above the surrounding surface to prevent surface water from running over or ponding on top of the casing. It should be noted that in areas subject to snowfall, flush-mount casings may have to be installed so that they are entirely flush with the ground surface as they may be damaged by snow plows.

Above-ground protective casings should also be vented or should have non-air tight caps. Road box installations should not be vented. Installation of additional guard pipes may be necessary around above-ground well completions in traffic areas. All new monitoring wells will include a locking well cap with locks that are keyed alike.

7.2.8 Well Numbering

The field personnel will number each well casing with an indelible marker or paint to identify the well. This is particularly important with nested or paired wells to distinguish between shallow and deep wells. The well should be labeled on both the outside of the protective casing and inside beneath the protective casing lid. Well identification numbers will be as specified in the FSP.

7.2.9 Measuring Point Identification

The project field personnel will mark the measuring point from which water level measurements will be made at the upper edge of the well casing. PVC wells can easily be notched with a pocket knife or saw, or can be marked with a waterproof marker on the outside of the well casing with an arrow pointing to the measuring point location. The measuring point is the point that will require surveying during the well elevation survey task.

7.2.10 Well Measurements

Upon completion, the following well measurements should be taken by field personnel and recorded on the Monitoring Well Construction Diagram (Figure 1):

- Depth to static water level if water level has stabilized (refer to ENSR SOP No. 101Pines – Water Level Measurements),
- Total length of well measured from top-of-well casing (refer to ENSR SOP No. 101Pines – Water Level Measurements),
- Height of well casing above ground surface,
- Height of protective casing above ground surface,
- Depth of bottom of protective casing below ground surface (may be estimated).

Well screen filter pack, bentonite seal and annular seal thicknesses and depths should also be recorded on the Monitoring Well Construction Diagram (Figure 1).

7.2.11 Disposal of Drilling Wastes

Drill cuttings and other disposable materials must be properly contained and disposed of. Site-specific requirements for collection and removal of these waste materials are outlined in the FSP. Containment of these materials should be performed by the drilling subcontractor.

7.2.12 Well Development

At some point after installation of a well and prior to use of the well for water level measurements or collection of water quality samples, development of the well shall be undertaken in accordance with ENSR SOP No. 7221Pines - Monitoring Well Development.

7.2.13 Well Elevation Survey

At the completion of the well installation program, all monitoring wells will be surveyed to provide, at a minimum, the location (x and y coordinates), and the top-of-casing measuring point elevation for water level monitoring purposes. Other surveyed points required by the FSP include ground surface elevation, top of protective casing elevation, and well coordinate position. Well elevation surveys will be conducted by a surveying subcontractor in accordance with the FSP.

8.0 DATA AND RECORDS MANAGEMENT

All field information will be recorded in the field logbook or on a field collection form by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the well drilling and installation process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the QAPP and/or FSP.

Certain quality control measures should be taken to ensure proper well completion.

- The borehole will be checked for total open depth, and extended by further drilling or shortened by backfilling, if necessary, before any well construction materials are placed.

- The water level will be checked during well installation to ensure that the positions of well screen, sand pack, and seal relative to water level conform to project requirements.

- The depth to the top of each layer of packing (i.e., sand, bentonite, grout) will be verified and adjusted if necessary to conform to project requirements before the next layer is placed.

- If water or other drilling fluids (for example, to control running sands) have been introduced into the boring during drilling or well installation, samples of these fluids may be required for analysis of chemical constituents of interest.

10.0 REFERENCES

ENSR SOP No. 101Pines – Water Level Measurements.

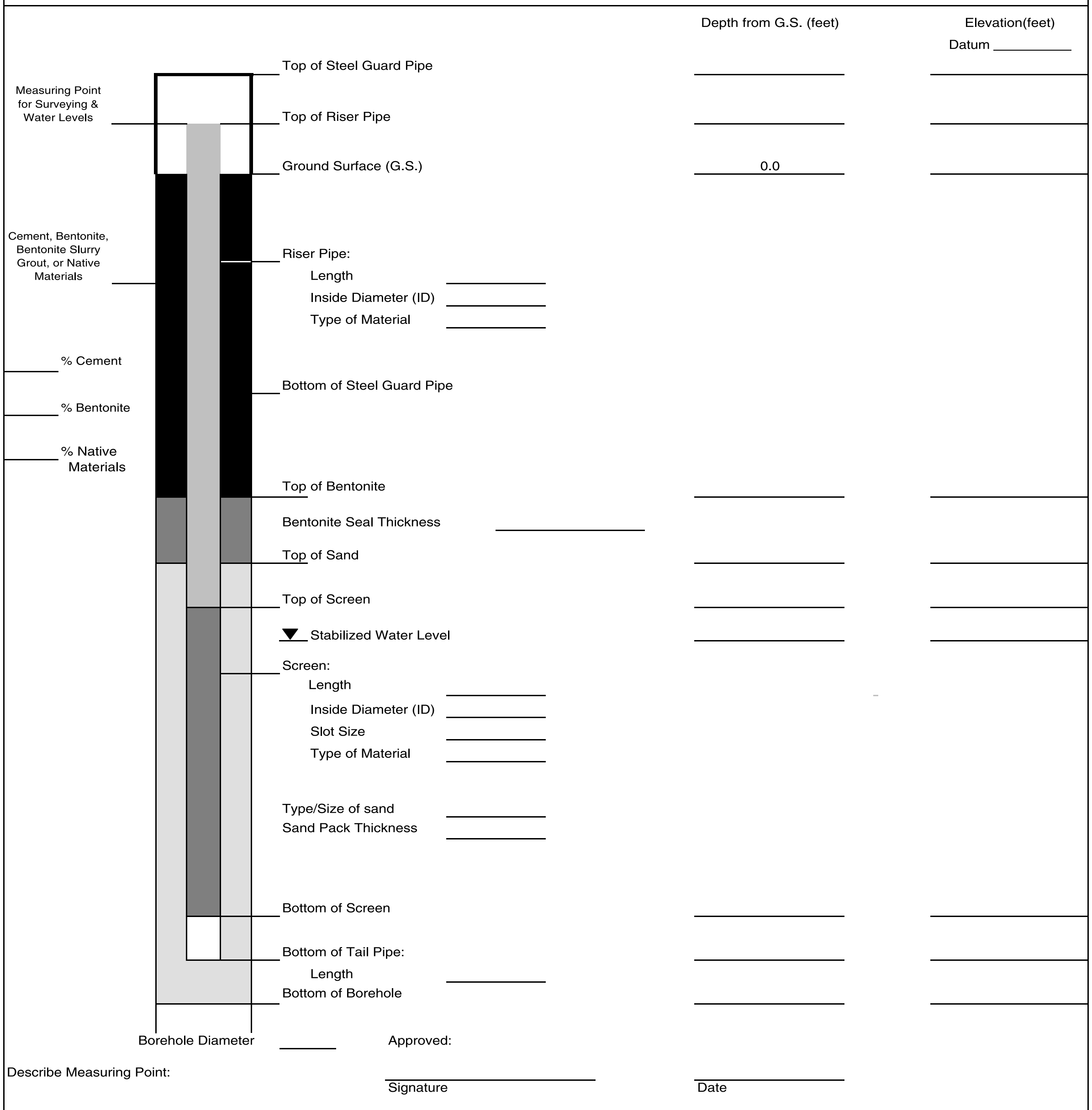
ENSR SOP No. 7221Pines - Monitoring Well Development.

ENSR SOP 7600Pines – Decontamination of Field Equipment. Revision 3.0.

FIGURE 1 – Example Monitoring Well Construction Detail

ENSR		
	Client:	WELL ID:
	Project Number:	
	Site Location:	*Date installed:*
	Well Location: *Coords:*	*Inspector:*
	Method:	*Contractor:*

MONITORING WELL CONSTRUCTION DETAIL



APPENDIX – GLOSSARY

Annulus: The measured width between the borehole wall and the outside of the well screen or riser pipe.

Bentonite Seal: A granular, chip, or pellet-size bentonite material that is often used to provide an annular seal above the well screen filter pack. This seal is typically installed dry followed by in-place hydration with or without the addition of water. Hydrated bentonite is sometimes used as a grout seal.

Bottom Cap/Plug: Threaded or slip-on cap placed at the bottom of the well prior to installation. Often serves as a sump for accumulation of silt which settles within the well. The measured length from the lowermost well screen slot to the bottom of the bottom cap is known as the sump or tail pipe portion of the well.

Centralizers: Stainless steel expansion clamps which, when fitted to well screens or riser pipe, expand to contact the borehole walls positioning the well centrally within the open borehole. Centralizers assist with even positioning and distribution of filter pack and sealant materials and assist with maintaining well plumbness.

Expansion Cap/Well Cap: Cap used to cover the opening at the top of the well riser pipe. Expansion caps are equipped with a rubber gasket and threaded wing nut which, when turned, provides a watertight seal. Expansion caps may also be locked, and generally are recommended for use with flush-constructed wells where road box protective casings are also used. Other well caps may include slip-on or threaded caps made of the same material as the well casing.

Filter Pack: A well-graded, clean sand or gravel placed around the well screen to act as a filter in preventing the entry of very fine soil particles into the well.

Grout Seal: A cement/bentonite mixture used to seal a borehole that has been drilled to a depth greater than the final well installation depth or to seal the remaining borehole annulus once the well has been installed. Occasionally, pure cement or pure bentonite is used as a grout seal.

Measuring Point: A selected point at the top of the well casing (riser pipe) used for obtaining periodic water-level measurements. The measuring point should consist of either a notch or indelibly marked point on the upper surface of the casing. Typically, the highest point on the casing (if not level) is used as the measuring point. The measuring point is also the point that is surveyed when well elevation data is obtained.

Protective Casing: A locking metal casing, placed around that portion of the well riser pipe that extends above the ground surface. The protective casing is generally cemented in place when the concrete pad is constructed around the well.

Riser Pipe: The section of unperforated well casing material used to connect the well screen with the ground surface. Frequently, it is made of the same material and has the same diameter as the well screen. Riser pipe is typically available pre-cleaned and pre-threaded for immediate use.

Road Box: A protective casing that is flush-mounted with the ground around a well installation. Road boxes are used in areas where the monitoring well cannot extend above the ground surface for traffic or security reasons. Road boxes usually require a special key to open.

Tremie Pipe: A small diameter pipe which fits in the open borehole annulus and is used to inject filter sands or hydrated seal materials under pressure.

Well Screen: That portion of the well casing material that is perforated in some manner so as to provide a hydraulic connection to the aquifer. Typically a well screen is purchased pre-slotted, pre-cleaned, and pre-threaded for immediate use.

Vent Hole: Small diameter hole drilled in the upper portion of the well riser pipe which provides atmospheric venting of the well. Allows for constant equilibration of the water level with changing atmospheric conditions. In flood-prone areas, or with flush-mount wells, vent holes should not be used.

ENSR INTERNATIONAL

Monitoring Well Development

SOP Number 7221Pines

Revision Number: 2.0

May 2005

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ENSR Project Manager
May 23, 2005

Debra L. McGrath

ENSR Project QA Officer
May 23, 2005

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CONTENTS

APPENDICES

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDW	Investigation Derived Waste
OSHA	Occupational Safety and Health Administration
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods used for developing newly installed monitoring wells and/or existing wells that may require redevelopment/rehabilitation. This SOP is applicable to any wells that require development in accordance with the Field Sampling Plan (FSP).

Monitoring well development and/or redevelopment is necessary for several reasons:

- To improve/restore hydraulic conductivity of the surrounding formations as they have likely been disturbed during the drilling process, or may have become partially plugged with silt;

- To remove drilling fluids (water, mud), when used, from the borehole and surrounding formations; and

- To remove residual fines from well filter materials and reduce turbidity of groundwater, therefore, reducing the chance of chemical alteration of groundwater samples caused by suspended sediments and provide representative groundwater samples.

2.0 SUMMARY OF METHOD

Well development generally involves withdrawal of an un-specified volume of water from a well using a pump, surge block or other suitable method such that, when completed effectively, the well is in good or restored hydraulic connection with the surrounding water bearing unit and is suitable for obtaining representative groundwater samples or for other testing purposes.

3.0 HEALTH AND SAFETY WARNINGS

Monitoring well development may involve chemical hazards associated with exposure to materials in the groundwater being investigated and physical hazards associated with use of well development equipment. When well development is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Potential interferences could result from cross-contamination between sample locations. Minimization of the cross-contamination will occur through the use of clean tools at each location, which will require decontamination of sampling equipment as per ENSR SOP No. 7600Pines – Decontamination of Field Equipment.

The process of installing a well necessarily disturbs the geologic formation. Wells will be developed appropriately as described in this SOP. The wells will be allowed to stabilize a minimum of two weeks after development before a well is sampled. In no cases will methods using air (e.g., air jetting) be used for well development on this project as they have a high potential to change geochemical conditions in the vicinity of the well.

5.0 PERSONNEL QUALIFICATIONS

Well development procedures vary in complexity. It is recommended that initial development attempts be supervised by more experienced personnel.

Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within the FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for proper well development, decontamination of equipment, as well as proper documentation in the field logbook or field forms (if appropriate).

6.0 EQUIPMENT AND SUPPLIES

Well development can be performed using a variety of methods and equipment. The specific method chosen for development of any given well is governed by the purpose of the well, well diameter and materials, depth, accessibility, geologic conditions, static water level in the well, and type of constituents present, if any.

The following list of equipment, each with their own particular application, may be used to develop and/or purge monitoring wells. In no cases will methods using air (e.g., air jetting) be used on this project as they have a high potential to change geochemical conditions in the vicinity of the well.

6.1 Bailer Purging

A bailer is used to purge silt-laden water from wells after using other devices such as a surge block. In some situations, the bailer can be used to develop a well by bailing and surging, often accompanied with pumping. A bailer can be used for purging in situations where the depth to static water is greater than 25 feet and/or where insufficient hydraulic head is available for use of other development methods.

6.2 Surge Block Development

Surge blocks are commercially available for use with Waterra™-type pumping systems or may be manufactured using a "plunger" attached to a rod or pipe of sufficient length to reach the bottom of the well. Well drillers usually can provide surge blocks if requested. A recommended design is shown in Figure 1.

6.3 Pump Development

A pump is often necessary to remove large quantities of silt-laden ground water from a well after using the surge block. In some situations, the pump alone can be used to develop the well and remove the fines by overpumping. Because the purpose of well development is to remove suspended solids from a well and the surrounding filter pack, the pump must be capable of moving some solids without damage. The preferred pump is a submersible pump, which can be used in both shallow and deep ground water situations. A centrifugal pump may be used in shallow wells, but will work only where the depth to static ground water is less than approximately 25 feet. Pumping may not be successful in low-yielding aquifer materials or in wells with insufficient hydraulic head.

6.4 Other Required Materials:

- Well Development Records (Figure 2)
- Boring and well construction logs (if available)
- Utility knife
- Plastic sheeting
- Buckets

- Paper towels
- Trash bags
- Power source (generator or 12-volt marine battery)
- Water level meter and/or well depth measurement device
- Water quality instrumentation to measure turbidity (i.e., nephelometer)
- Instrument calibration solutions
- Equipment decontamination supplies (as required by ENSR SOP No. 7600Pines – Decontamination of Field Equipment)
- Health and safety supplies (as required by the HASP)
- Appropriate containers and materials to manage investigation-derived waste (IDW) (as specified in the FSP)
- Approved plans (e.g., HASP, QAPP, FSP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

Well completion diagrams should be reviewed to determine well construction characteristics. Formation characteristics should also be determined from review of available boring logs.

Well development, similar to groundwater sampling, should be conducted in as clean an environment as possible. This usually requires, at a minimum, placing sheet plastic on the ground to provide a clean working area for development equipment.

Provisions should be in place for collection and management of IDW, specifically well development water and miscellaneous expendable materials generated during the development process. The collection of IDW in drums or tanks may be required depending on project-specific requirements. The FSP specifies the requirements for IDW containment.

The water level and well depth should be measured in accordance with ENSR SOP No. 101Pines – Water Level Measurements and written on the Well Development Record (Figure 2). This information is used to calculate the volume of standing water (i.e., the well volume) within the well.

Drilling fluids such as mud or water, if used during the drilling and well installation process, should be removed during the well development procedure. It is recommended that a minimum of 3 times the volume of added fluid be removed from the well during development. If the quantity of added fluid is not known or cannot be reasonably estimated, removal of a minimum of 20 well volumes of water is recommended during the development procedure.

7.2 Development Procedure

7.2.1 Development Method Selection

The construction details of each well shall be used to define the most suitable method of well development. Some consideration should be given to the potential concentrations of constituents in each well as this will impact IDW containment requirements.

The criteria for selecting a well development method include well diameter, total well depth, static water depth, screen length, the likelihood and potential concentrations of constituents, and characteristics of the geologic formation adjacent to the screened interval.

The limitations, if any, of a specific procedure are discussed within each of the following procedures.

7.2.2 General Water Quality Measurements (optional)

Measurements for water quality parameters such as specific conductance may be monitored periodically during development using the available water quality instruments (e.g., ENSR SOP No. 105Pines - Operation and Calibration of the YSI 6920 Multi-Parameter Water Quality Monitor). These measurements may be used to determine whether or not well development is proceeding efficiently, determine whether or not the development process is effective with any given well and, potentially, may identify well construction irregularities (i.e., grout in well, poor well screen slot-size selection). Water quality parameters will be recorded on the Well Development Record (Figure 2).

7.2.3 Turbidity

Turbidity will be monitored during well development to monitor the progress of development. Visual observations on turbidity, such as silty or cloudy water, should be noted in the Well Development Record (Figure 2). Turbidity should also be measured quantitatively using a nephelometer. Turbidity should be measured a minimum of three times during development, including at the completion of development. All turbidity readings will be recorded in the Well Development Record (Figure 2).

7.2.4 Bailer Procedure

As stated previously, bailers shall preferably not be used for well development but may be used in combination with a surge block to remove silt-laden water from the well.

- When using a bailer to purge well water; select the appropriate bailer, then tie a length of bailer cord onto the end of it.

- Lower the bailer into the screened interval of the monitoring well. Silt, if present, will generally accumulate within the lower portions of the well screen.

- The bailer may be raised and lowered repeatedly in the screened interval to further simulate the action of a surge block and pull silt through the well screen.

- Remove the bailer from the well and empty it into the appropriate storage container.

- Continue surging/bailing the well until sediment-free water is obtained. If moderate to heavy siltation is still present, the surge block procedure should be repeated and followed again with bailing. If it is not possible to further reduce the visible turbidity, the well will be purged a maximum of four hours.

- Check turbidity and any other water quality parameters, periodically.

7.2.5 Surge Block Procedure

A surge block effectively develops most monitoring wells. This device first forces water within the well through the well screen and out into the formation, and then pulls water back through the screen into the well along with fine soil particles. Surge blocks may be manufactured to meet the design criteria shown in the example (Figure 1) or may be purchased as an adaptor to fit commercially available well purging systems such as the Waterra™ system.

- Insert the surge block into the well and lower it slowly to the level of static water. Start the surge action slowly and gently above the well screen using the water column to transmit the surge action to the screened interval. A slow initial surging, using plunger strokes of approximately 3 feet, will allow material that is blocking the screen to separate and become suspended.

- After 5 to 10 plunger strokes, silt-laden water will be removed from the well using a pump integrated with the surge block, or removing the surge block to purge the well using a pump or bailer. The returned water should be heavily laden with suspended silt and clay particles. Discharge the purged water into the appropriate storage container.

- Repeat the process. As development continues, slowly increase the depth of surging to the bottom of the well screen. For monitoring wells with long screens (greater than 10 feet) surging should be undertaken along the entire screen length in short intervals (2 to 3 feet) at a time. Continue this cycle of surging and purging until the water yielded by the well is free of visible suspended material. If it is not possible to further reduce the visible turbidity, the well will be purged a maximum of four hours.

- Check turbidity and any other water quality parameters periodically.

7.2.6 Pump Procedure

Well development using only a pump is most effective in monitoring wells that will yield water continuously. Theoretically, pumping will increase the hydraulic gradient and velocity of groundwater near the well by drawing the water level down. The increased velocity will move residual fine soil particles into the well and clear the well screen of this material. Effective development cannot be accomplished if the pump has to be shut off to allow the well to recharge.

- When using a submersible pump or surface pump, set the intake of the pump or intake line in the center of the screened interval of the monitoring well.

- Pump a minimum of three well volumes of water from the well and raise and lower the pump line through the screened interval to remove any silt/laden water.

- Continue pumping water from the well until sediment-free water is obtained. This method may be combined with the manual surge block method if well yield is not rapid enough to extract silt from the surrounding formations. If it is not possible to further reduce the visible turbidity, the well will be purged a maximum of four hours.

- Check turbidity and any other water quality parameters periodically.

7.3 Equipment Decontamination

All equipment that comes into contact with groundwater (e.g., surge block) will be decontaminated in accordance with ENSR SOP No. 7600Pines – Decontamination of Field Equipment before moving to the next location. The bailer should be properly discarded and disposed of in accordance with procedures for managing IDW outlined in the FSP.

8.0 DATA AND RECORDS MANAGEMENT

All field information will be recorded in the field logbook or on a field collection form by field personnel. In addition, a field project logbook will be maintained detailing any problems or unusual conditions that may have occurred during the development process.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

Field personnel should follow specific quality assurance guidelines as outlined in the Quality Assurance Project Plan (QAPP) and/or FSP.

A well will have been successfully developed when one or more of the following criteria are met:

- The sediment load in the well has been eliminated or greatly reduced. Use of a nephelometer is required during the well development procedure to measure water turbidity if meeting a specific turbidity value is required by the FSP. Attaining low turbidity values in fine-grained formations may be difficult to achieve.

- If it is not possible to reduce turbidity to acceptable levels, the well will be developed for a maximum of four hours.

10.0 REFERENCES

ENSR SOP No. 105Pines - Operation and Calibration of the YSI 6920 Multi-Parameter Water Quality Monitor.

ENSR SOP No. 101Pines – Water Level Measurements.

ENSR SOP No. 7600Pines – Decontamination of Field Equipment. Revision 3.0.

FIGURE 1 – RECOMMENDED SURGE BLOCK DESIGN

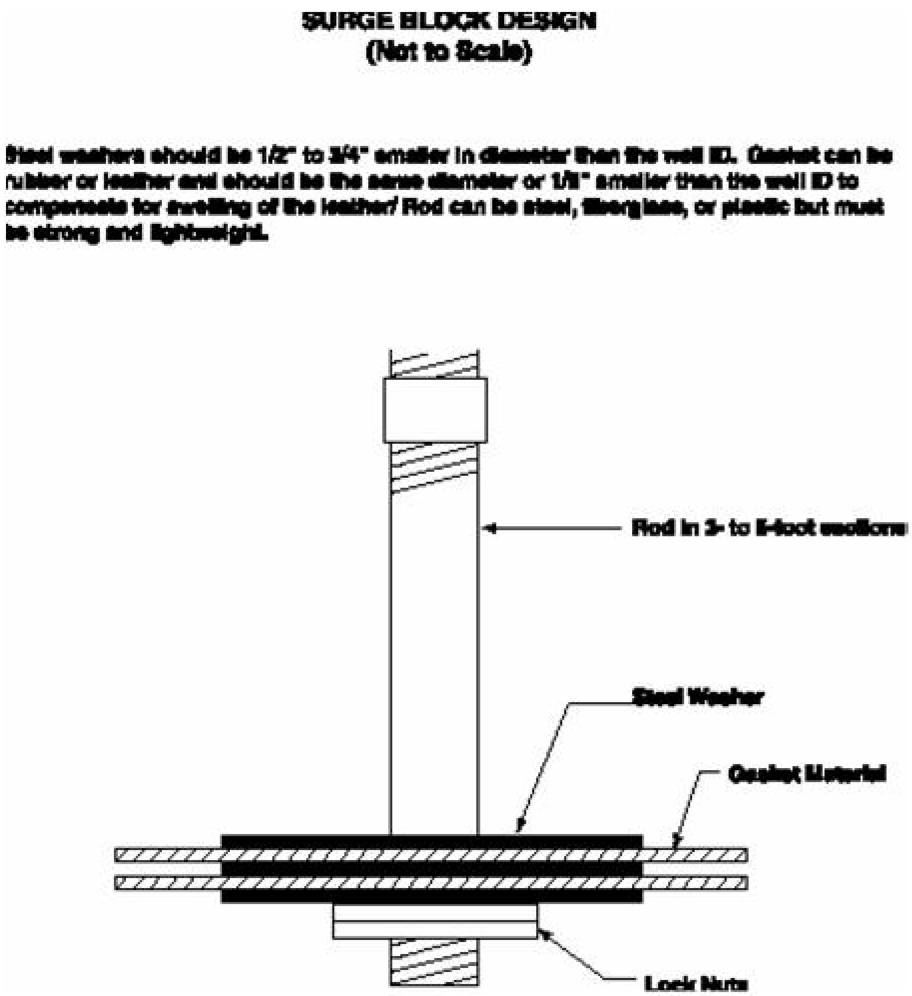


FIGURE 2 – EXAMPLE WELL DEVELOPMENT RECORD

ENSR

Well/Piez. ID:

Well/Piezometer Development Record

Client: ____________________

Project No: ____________________ Date: __________ Developer: ____________________

Site Location: ____________________

Well/Piezometer Data

Well ☐ Piezometer ☐ Diameter __________ Material __________

Measuring Point Description __________

Depth to Top of Screen (ft.) __________

Depth to Bottom of Screen (ft.) __________

Total Well Depth (ft.) __________

Depth to Static Water Level (ft.) __________

Geology at Screen Interval (if known) __________

Time of Water Level Measurement __________

Calculate Purge Volume (gal.) __________

Disposal Method __________

Headspace __________

Original Well Development ☐ Redevelopment ☐ Date of Original Development __________

DEVELOPMENT METHOD ____________________

PURGE METHOD ____________________

Time	Total Volume Purged (gal.)	Flow Rate (gpm)	Turbidity (NTU)	Color	pH	Temp	Other

ACCEPTANCE CRITERIA (from workplan)
Minimum Purge Volume Required _____ gallons
Maximum Turbidity Allowed _____ NTUs
Stabilization of parameters _____%

	Yes	No	N/A
Has required volume been removed	☐	☐	☐
Has required turbidity been reached	☐	☐	☐
Has parameters stabilized	☐	☐	☐

If no or N/A explain below:

____

Signature ____________________ Date: __________

APPENDIX A – GLOSSARY

Bridging: A condition within the filter pack outside the well screen whereby the smaller particles are wedged together in a manner that causes blockage of pore spaces.

Hydraulic Conductivity: a characteristic property of aquifer materials which describes the permeability of the material with respect to flow of water.

Hydraulic Connection: A properly installed and developed monitoring well should have good hydraulic connection with the aquifer. The well screen and filter material should not provide any restriction to the flow of water from the aquifer into the well.

Permeability Test: Used to determine the hydraulic conductivity of the aquifer formation near a well screen. Generally conducted by displacing the water level in a well and monitoring the rate of recovery of the water level as it returns to equilibrium. Various methods of analysis are available to calculate the hydraulic conductivity from these data.

Static Water Level: The water level in a well that represents an equilibrium or stabilized condition, usually with respect to atmospheric conditions in the case of monitoring wells.

Well Surging: That process of moving water in and out of a well screen to remove fine sand, silt and clay size particles from the adjacent formation.

Well Purging: The process of removing standing water from a well to allow surrounding formation water to enter the well.

Well Screen: That portion of the well casing material that is perforated in some manner so as to provide a hydraulic connection to the aquifer. The perforated, or slotted, portion of a well is also known as the screened interval.

Packaging and Shipment of Environmental Samples

SOP Number 7510Pines

Revision Number: 4.0

September 2005

Lesa M. Bradley

ENSR Project Manager
September 2, 2005

Debra L. McGrath

ENSR Project QA Officer
September 2, 2005

ENSR Corporation
September 2005
Pines Area of Investigation

CONTENTS

LIST OF ACRONYMS

COC	Chain-of-Custody
DOT	Department of Transportation
HASP	Health and Safety Plan
OSHA	Occupational Safety and Health Adminstration
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RCRA	Resource Conversation and Recovery Act
RI	Remedial Investigation
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the procedures associated with the packaging and shipment of environmental samples consisting of water, soil, and sediment submitted for routine environmental testing. Environmental samples are not considered a Resource Conservation and Recovery Act (RCRA) classified hazardous waste by definition; therefore, more stringent RCRA and Department of Transportation (DOT) regulations regarding sample transportation do not apply. Environmental samples do, however, require fairly stringent packaging and shipping measures to ensure sample integrity as well as safety for those individuals handling and transporting the samples.

This SOP is designed to provide a high degree of certainty that environmental samples will arrive at their destination intact. This SOP assumes that samples will often require shipping overnight by a commercial carrier service; therefore, the procedures are more stringent than may be necessary if a laboratory courier is used or if samples are transported directly to their destination by a field personnel. Should either of the latter occur, the procedures may be modified to reflect a lesser degree of packaging requirements.

2.0 SUMMARY OF METHOD

Sample packaging and shipment involves the placement of individual sample containers into a cooler or other similar shipping container and placement of packing materials and coolant in such a manner as to isolate the samples, maintain the required temperature, and to limit the potential for damage to sample containers when the cooler is transported.

3.0 HEALTH AND SAFETY WARNINGS

Sampling personnel should be aware that packaging and shipment of samples involves potential exposure and physical hazards primarily associated with handling of occasional broken sample containers and lifting of heavy objects. Adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Sample containers with presumed high constituent concentrations should be isolated within their own cooler with each sample container placed into a zipper-lock bag.

5.0 PERSONNEL QUALIFICATIONS

Sample packaging and shipment is a relatively simple procedure requiring minimal training and a minimal amount of equipment. It is recommended that initial attempts be supervised by more experienced personnel.

Field personnel should be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous waste materials may be present.

It is the responsibility of the field personnel to be familiar with the procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within the FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are also responsible for proper documentation in the field logbook.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Sample coolers
- Sample containers
- Shipping labels
- Chain-of-custody (COC) form (Figure 1)
- Custody tape (Figure 2)
- Bubble wrap
- Vermiculite (granular), or styrofoam pellets
- Ice
- Temperature blank
- Transparent tape, or rubber bands
- Fiber tape
- Duct tape

- Utility knife
- Zipper-lock plastic bags
- Trash bags
- Health and safety supplies (as required by the HASP)
- Field project logbook/pen

7.0 METHODS

7.1 Preparation

The extent and nature of sample containerization will be governed by the type of sample, and the most reasonable projection of the sample's hazardous nature and constituents. U.S. Environmental Protection Agency (USEPA) regulations (40 CFR Section 261.4(d)) specify that samples of solid waste, water, soil or air, collected for the sole purpose of testing, are exempt from regulation under RCRA when any of the following conditions are applicable:

- Samples are being transported to a laboratory for analysis;
- Samples are being transported to the collector from the laboratory after analysis;
- Samples are being stored (1) by the collector prior to shipment for analyses, (2) by the analytical laboratory prior to analyses, or (3) by the analytical laboratory after testing but prior to return of sample to the collector or pending the conclusion of a court case.

7.1.1 Laboratory Notifications

Prior to sample collection, the ENSR Remedial Investigation (RI) Task Manager or designee must notify the laboratory project manager of the number, type, and approximate collection and shipment dates for the samples. If the number, type, or date of sample shipment changes due to program changes that may occur in the field, the ENSR RI Task Manager or alternate must notify the laboratory of the changes. Additional notification from the field is often necessary when shipments are scheduled for weekend delivery.

7.1.2 Cooler Inspection and Decontamination

Laboratories will often re-use coolers. Every cooler received at a project location should be inspected for condition and cleanliness. Any coolers that exhibit cracked interiors or exterior linings/panels or hinges should be discarded because the insulating properties of the coolers would be considered compromised. Any coolers missing one or both handles should also be discarded if replacement handles (i.e., knotted rope handles) can not be fashioned in the field.

The interior and exterior of each cooler should be inspected for cleanliness before using it. Excess strapping tape and old shipping labels should be removed. If the cooler interior exhibits visible contamination or odors it should not be used. Drain plugs should be sealed on the inside with duct tape.

7.2 Sample Packaging

7.2.1 Place plastic bubble wrap matting over the base of each cooler or shipping container as needed. A 2- to 3-inch thick layer of vermiculite may be used as a substitute base material.

7.2.2 Insert a clean trash bag into the cooler to serve as a liner.

7.2.3 Check that each sample container is sealed, labeled legibly, and is externally clean. Re-label and/or wipe bottles clean if necessary. Clear tape should be placed over the labels to protect them and keep them from falling off the container. Wrap each sample bottle individually with bubble wrap secured with tape or rubber bands. For aqueous samples in glass containers, each sample should be sealed in a zipper-lock bag to prevent leakage and cross-contamination in the case of breakage. Place bottles into the cooler in an upright single layer with approximately one inch of space between each bottle. Do not stack bottles or place them in the cooler lying on their side. If plastic and glass sample containers are used, alternate the placement of each type of container within the cooler so that glass bottles are not placed side by side.

7.2.4 Insert the cooler temperature blank supplied by the laboratory into each cooler (if any).

7.2.5 Place additional vermiculite, bubble wrap, and/or styrofoam pellet packing material throughout the voids between sample containers within each cooler to a level that meets the approximate top of the sample containers. Packing material may require tamping by hand to reduce the potential for settling.

7.2.6 Double bag cubed ice in heavy duty zipper-lock plastic bags, close the bags, and distribute the bagged ice in a layer over the top of the samples. Loose ice should never be used. Cold packs should be used only if the samples are chilled before being placed in the cooler.

7.2.7 Add additional bubble wrap/styrofoam pellets or other packing materials to fill the balance of the cooler or container.

7.2.8 Obtain two pieces of COC tape as shown in Figure 2 and enter the custody tape numbers in the appropriate place on the COC form (Figure 1). Sign and date the COC tape.

7.2.9 Complete the COC form per ENSR SOP No. 1007Pines – Chain-of-Custody Procedures. If shipping the samples involves use of a third party commercial carrier service, sign the COC record thereby relinquishing custody of the samples. Shippers should not be asked to sign COC records. If a laboratory courier is used, or if samples are transported to the laboratory by field personnel, the receiving party should accept custody and sign the COC records. Remove the last copy from the multi-form COC and retain it with other field notes. Place the original (with remaining copies) in a zipper-lock plastic bag and tape the bag to the inside lid of the cooler or shipping container.

7.2.10 Close the lid of the cooler or the top of the shipping container.

7.2.11 Place the COC tape at two different locations (i.e., one tape on each side) on the cooler or container lid and overlap with transparent packaging tape.

7.2.12 Packaging tape should be placed entirely around the sample shipment containers. A minimum of two full wraps of packaging tape will be placed at least two places on the cooler/container.

7.2.13 Repeat the above steps for each cooler or shipping container.

7.3 Sample Shipping

Transport the cooler/container to the package delivery service office or arrange for package pick-up at the site. Fill out the appropriate shipping form or airbill and affix it to the cooler/container. Some courier services may use multi-package shipping forms where only one form needs to be filled out for all packages going to the same destination. If not, a separate shipping form should be used for each cooler/container. The receipt for package tracking purposes should be kept in the project files, in the event a package becomes lost.

Each cooler/container also requires a shipping label that indicates point of origin and destination. This will aid in recovery of a lost cooler/container if a shipping form gets misplaced.

Never leave coolers/containers unattended while waiting for package pick-up.

Airbills or waybills will be maintained as part of the custody documentation in the project files.

7.4 Sample Receipt

Upon receipt of the samples, the analytical laboratory will open the cooler or shipping container and will sign "received by laboratory" on each COC form. The laboratory will verify that the COC tape has not been broken previously and that the tape number corresponds with the number on the COC record. The laboratory will note the condition of the samples upon receipt and will identify any discrepancies between the contents of the cooler/container and COC. The analytical laboratory will then forward the back copy of the COC record to the project Quality Assurance (QA) Officer to indicate that sample transmittal is complete.

8.0 DATA AND RECORDS MANAGEMENT

Documentation supporting sample packaging and shipment consists of COC records and shipping records. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

The potential for samples to break during transport increases greatly if individual containers are not snugly packed into the cooler. Packed coolers may be lightly shake-tested to check for any loose bottles. The cooler should be repacked if loose bottles are detected.

Environmental samples are generally shipped so that the samples are maintained at a temperature of approximately 4°C. Temperature blanks may be required for some projects as a quality assurance check on shipping temperature conditions. These blanks usually are supplied by the laboratory and consist of a 40-ml vial or plastic bottle filled with tap water. Temperature blanks should be placed near the center of the cooler.

10.0 REFERENCES

ENSR SOP No. 1007Pines – Chain-of-Custody Procedures.

FIGURE 1 - Example Chain of Custody Form

M901376

ENSR **CHAIN OF CUSTODY RECORD** Page ____ of ____

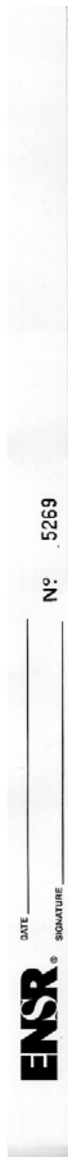
Client/Project Name:	Project Location:
Project Number:	Field Logbook No.:
Sampler: (Print Name) /Affiliation:	Chain of Custody Tape No.:
Signature:	Send Results/Report to:

Analysis Requested

Field Sample No./ Identification	Date	Time	Grab	Comp	Sample Container (Size/Mat'l)	Sample Type (Liquid, Sludge, Etc.)	Preservative	Field Filtered							Lab I.D.	Remarks

Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	Analytical Laboratory (Destination): ENSR 4303 W. LaPorte Ave. Fort Collins, CO 80521 (970) 416-0916
Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	
Relinquished by: (Print Name) Signature:	Date: Time:	Received by: (Print Name) Signature:	Date: Time:	Serial No.

FIGURE 2 - Example Chain of Custody Tape



Decontamination of Field Equipment

SOP Number 7600Pines

Revision Number: 3.0

May 2005

ENSR Project Manager
May 23, 2005

ENSR Project QA Officer
May 23, 2005

ENSR Corporation
May 2005
Pines Area of Investigation

Decontamination of Field Equipment

CONTENTS

LIST OF ACRONYMS

FSP	Field Sampling Plan
HASP	Health and Safety Plan
IDW	Investigation Derived Waste
OSHA	Occupational Safety and Health Administration
QC	Quality Control
SOP	Standard Operating Procedure
QAPP	Quality Assurance Project Plan

1.0 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the methods to be used for the decontamination of field equipment used in the collection of environmental samples. Field equipment for decontamination may include a variety of items used in the field for monitoring or for collection of soil, sediment, and/or water samples, such as water level meters, water quality monitoring meters (turbidity meter, multi-parameter meter), split-spoon samplers, trowels, scoops, spoons, and pumps. Heavy equipment such as drill rigs also requires decontamination, usually in a specially constructed temporary decontamination area.

Decontamination is performed as a quality assurance measure and a safety precaution. Improperly decontaminated sampling equipment can lead to misinterpretation of environmental data due to interference caused by cross-contamination between samples or sample locations through use of contaminated equipment. Decontamination also protects field personnel from potential exposure to hazardous materials on equipment.

This SOP emphasizes decontamination procedures to be used for decontamination of reusable field equipment. Dedicated or disposable equipment will not need to be decontaminated.

2.0 SUMMARY OF METHOD

Decontamination is accomplished by manually scrubbing, washing, or spraying equipment with detergent solutions, tap water, distilled/deionized water, and/or solvents.

Generally, decontamination of equipment is accomplished at each sampling site between collection points. Waste decontamination materials such as spent liquids and solids will be collected and managed as investigation derived waste (IDW) for later management and/or disposal (refer to procedures outlined in the Field Sampling Plan (FSP)). All decontamination materials, including wastes, should be stored in a central location so as to maintain control over the materials used or produced throughout the investigation program.

3.0 HEALTH AND SAFETY WARNINGS

Decontamination procedures may involve chemical exposure hazards associated with exposure to soil, water, or sediment and may involve physical hazards associated with decontamination materials. When decontamination is performed, adequate health and safety measures must be taken to protect field personnel. These measures are addressed in the project Health and Safety Plan (HASP). All work will be conducted in accordance with the HASP.

4.0 INTERFERENCES

Equipment decontamination should be performed a safe distance away from the sampling area so as not to interfere with sampling activities, but close enough to the sampling area to maintain an efficient working environment.

5.0 PERSONNEL QUALIFICATIONS

Decontamination of field equipment is a relatively simple procedure requiring minimal training. It is recommended that the initial decontamination of field equipment be supervised by more experienced personnel. Field personnel must be health and safety certified as specified by the Occupational Safety and Health Administration (OSHA) (29 CFR 1910.120(e)(3)(i)) to work on sites where hazardous materials may be present.

It is the responsibility of field personnel to be familiar with the decontamination procedures outlined within this SOP, quality assurance, and health and safety requirements outlined within FSP, Quality Assurance Project Plan (QAPP), and HASP. Field personnel are responsible for decontamination of field equipment and for proper documentation in the field logbook.

6.0 EQUIPMENT AND SUPPLIES

General field supplies include the following items:

- Decontamination agents (which are specified in the FSP):
  - DETERGENT8®, or other non-phosphate and non-borate biodegradable detergent;
  - Tap water;
  - Distilled/deionized water; and/or
  - 10% nitric acid solution.
- Health and safety supplies (as required by the HASP)
- Chemical-free paper towels
- Waste storage containers: drums, 5-gallon buckets with covers, plastic bags
- Cleaning containers: plastic buckets or tubs
- Cleaning brushes
- Pressure sprayers
- Squeeze bottles

- Plastic sheeting
- Aluminum foil
- Zipper-lock bags
- Approved plans (e.g., HASP, QAPP, FSP)
- Field project logbook/pen

7.0 METHODS

7.1 General Preparation

7.1.1 New materials, such as well materials, are generally assumed to be clean and decontamination is not anticipated. However, they should be inspected and if they appear to be dirty, should be decontaminated.

Field equipment that is not frequently used should be wrapped in aluminum foil, shiny side out, and stored in a designated "clean" area. Small field equipment can also be stored in zipper-lock plastic bags to eliminate the potential for contamination. Field equipment should be inspected and decontaminated prior to use if the equipment appears dirty.

7.1.2 Heavy equipment (drill rigs, Geoprobes®, excavators) should be decontaminated upon arrival at the Area of Investigation, prior to beginning any work.

7.1.2 A decontamination station will be established within an area that is convenient to each sampling location. If single samples will be collected from multiple locations, then a centralized decontamination station or a portable decontamination station may be established.

7.1.3 One or more IDW containment stations should be established at this time also. In general, decontamination solutions are discarded as IDW between sampling locations.

7.2 Decontamination for Inorganic (Metals) Analyses

7.2.1 This procedure applies to equipment used in the collection of environmental samples submitted for inorganic constituent analysis. Examples of relevant items of equipment include split-spoons, trowels, scoops/spoons, and other small items. Submersible pump decontamination procedures are outlined in Section 7.4.

7.2.2 Decontamination is to be performed before sampling events and between sampling points, unless otherwise noted in the FSP.

7.2.3 After a sample has been collected, remove all gross contamination from the equipment or material by brushing and then rinsing with available tap water. This initial step may be completed using a 5-gallon bucket filled with tap water. A water pressure sprayer may also be used to remove solids and/or other contamination.

7.2.4 Wash the equipment with a non-phosphate and non-borate detergent and tap water solution. This solution should be kept in a 5-gallon bucket with its own brush.

7.2.5 Rinse with tap water or distilled/deionized water until all detergent and other residue is washed away. This step can be performed over an empty bucket using a squeeze bottle or pressure sprayer.

7.2.6 Rinse with 10% nitric acid.

7.2.7 Rinse with distilled/deionized water to remove any residual acid.

7.2.8 Allow the equipment to air-dry in a clean area or blot with chemical-free paper towels before reuse. Wrap the equipment in aluminum foil with the shiny side out and/or seal it in a zipper-lock plastic bag if it will not be reused immediately.

7.2.9 Dispose of soiled materials and spent solutions in the designated IDW disposal containers.

7.3 Decontamination of Submersible Pumps

7.3.1 This procedure will be used to decontaminate submersible pumps before and between groundwater sample collection points. This procedure applies to both electric submersible and bladder pumps. This procedure does not apply to discharge tubing if it will be reused between sampling points (see section 7.3.8 below).

7.3.2 Prepare the decontamination area if pump decontamination will be conducted next to the sampling point. If decontamination will occur at another location, the pump may be removed from the well and placed into a clean trash bag for transport to the decontamination area. Pump decontamination is easier with the use of 3-foot tall pump cleaning cylinders (i.e., Nalgene cylinder) for the various cleaning solutions, although the standard bucket rinse equipment may be used.

7.3.3 Once the decontamination station is established, the pump should be removed from the well and the discharge tubing and power cord coiled by hand as the equipment is removed. If any of the equipment needs to be put down temporarily, place it on a plastic sheet (around well) or in a clean trash bag. If a disposable discharge line is used it should be removed and discarded at this time.

7.3.4 As a first step in the decontamination procedure, use a pressure sprayer with tap water to rinse the exterior of the pump and power cord as necessary. Collect the rinsate and handle as IDW.

7.3.5 Place the pump into a pump cleaning cylinder or bucket containing a detergent solution (phosphate-free, borate-free detergent in tap water). Holding the power cord, pump solution through the pump system. A minimum of one gallon of detergent solution should be pumped through the system. Collect the rinsate and handle as IDW.

7.3.6 Remove the pump from the cylinder/bucket and if the pump is reversible, place the pump in the reverse mode to discharge all removable water from the system. If the pump is not reversible the pump and discharge line should be drained by hand as much as possible. Collect the rinsate and handle as IDW.

7.3.7 Using a pressure sprayer with distilled/deionized water, rinse the exterior of the pump and power cord thoroughly, shake all excess water, then place the pump system into a clean trash bag for storage. If the pump system will not be used immediately, the pump itself should be wrapped with aluminum foil before placing it into the bag.

7.3.8 If tubing will be reused between locations, the tubing will also need to be decontaminated. The tubing will remain attached to the pump and the decontamination steps (7.3.4 through 7.3.7) above will be followed. Additional volume of rinsate and distilled/deionized water will be used to compensate for the volume within the tubing. At a minimum, the volume of rinsate should be three times the capacity of the tubing.

7.4 Decontamination of Large Equipment

7.4.1 A temporary decontamination pad may be established for decontamination of heavy equipment. This pad may include a membrane-lined and bermed area large enough to drive heavy equipment (e.g., drill rig, backhoe) onto with enough space to spread other equipment and to contain overspray. Usually a small sump is necessary to collect and contain rinsate (a pump is used to remove these wastes from the sump). A water supply and power source is also necessary to run steam cleaning and/or pressure washing equipment.

7.4.2 Upon arrival at the Area of Investigation, all heavy equipment (such as drill rigs) should be thoroughly cleaned. This can be accomplished by steam cleaning or high pressure water wash and manual scrubbing.

Between each sample location (i.e., between boreholes), heavy equipment that has been in the ground must be cleaned by steam cleaning or high pressure water wash and manual scrubbing. This may be performed at the decontamination pad or in the vicinity of the drilling location.

8.0 DATA AND RECORDS MANAGEMENT

Specific information regarding decontamination procedures should be documented in the project-specific field logbook. Documentation within the logbook should thoroughly describe the construction of any decontamination facility and the decontamination steps implemented in order to show compliance with the FSP. Decontamination events should be logged when they occur with the following information documented:

- Date, time, and location of each decontamination event
- Equipment decontaminated
- Method
- Solvents and/or acids used
- Notable circumstances
- Identification of equipment rinsate blanks
- Management of decontamination fluids
- Method, date, and time of equipment blank collection
- Disposition of IDW

Repetitive decontamination of small items of equipment does not need to be logged each time the item is cleaned.

The records generated in this procedure will become part of the permanent record supporting the associated field work. All documentation will be retained in the project files following project completion.

9.0 QUALITY CONTROL AND QUALITY ASSURANCE

General guidelines for quality control check of field equipment decontamination usually require the collection of quality control (QC) samples such as equipment rinsate blanks. These requirements should be outlined in the QAPP and FSP.

Equipment rinsate blanks are generally made by pouring laboratory-supplied deionized water into, over, or through the freshly decontaminated sampling equipment and then transferring this water into a sample container. Equipment rinsate blanks should then be labeled as a sample (as per the QAPP and FSP) and submitted to the laboratory to be analyzed for the same parameters as the associated sample, or an appropriate subset thereof. Equipment rinsate blank sample numbers, as well as collection method, time and location should be recorded in the field logbook.

10.0 REFERENCES

Not applicable.

ATTACHMENT C

LABORATORY INSPECTION OF SUPPLIES

GENERAL ENGINEERING LABORATORIES, LLC

QUALITY ASSURANCE PLAN

(GL-QS-B-001 REVISION 16)

PROPRIETARY INFORMATION

Quality Assurance Plan Approval Signatures:

GEL's Document Control Officer certifies this document to be a true copy of the fully executed original.

AEJ

Prepared by:
General Engineering Laboratories, LLC

Guidelines for the required calibration and evaluation of this equipment are discussed in Section 7.

We perform radiochemical and bioassay analytical services in accordance with the instrumentation and reference methods approved by the Department of Energy (DOE), the Environmental Measurements Lab (EML), the Environmental Protection Agency (EPA), ASTM, and Los Alamos Health and Environmental Chemistry (LAHEC). Modifications to these methods may be appropriate as a result of Performance Based Measurement Systems (PBMS).

SOPs are used to describe our procedures for all routine analyses performed by our labs. These procedures include step-by-step instructions for sample collection, storage, preparation, analysis, instrument calibration, quality control, disposal, and data reporting.

5.3 Procurement and Control of Purchased Items

Materials and services that affect the quality of our products are designated as Quality Materials and Services and are only purchased from approved suppliers. We approve and document suppliers according to GL-QS-E-001 for the Conduct of Quality Audits.

At GEL, we maintain documentation of specific quality requirements for Quality Materials and Services. Records that document the quality of a product or service may include:

- certificates of analysis and traceability
- verifications of chemical quality
- inspections of equipment or materials
- verifications or inspections of vendor product specifications

Our procedure for requisitioning supplies, instruments, equipment and other common use material is described in GL-RC-E-002 for Material Requisition. These requests typically include:

- The date and name of person(s) requesting materials
- Account, department, project number to which the material is to be billed
- Recommended supplier or vendor
- Additional information necessary to expedite the purchase request
- Specifications that could affect the quality of products and services
- Vendor's material part number
- Amount of material needed
- Description of material
- Cost per unit
- Person(s) authorizing the purchase
- Time frame in which the material is needed

The equipment, instruments and reference materials we purchase are inspected upon receipt in accordance with GL-RC-E-001 for the Receipt and Inspection of Material and Services. This inspection is to verify that procured items meet the acceptance criteria defined in the procurement documentation. Staff performing initial inspection routinely:

- Open and inspect all items for damage
- Compare the items with the issued purchase order or contract for catalog or part number, description or procurement specification, quality requirement, and acceptance criteria
- Label items with a limited shelf life with the date received
- Determine if the items conform to the specifications agreed to by the vendor.

The individual responsible for the technical acceptance of the item provides procurement and receiving staff with the proper acceptance documentation. Items found not to conform to quality standards are returned to the supplier, identified as nonconforming or disposed according to the established procedures in GL-QS-E-004 for Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items.

Columbia Analytical Services INC.

An Employee - Owned Company

QUALITY ASSURANCE MANUAL

1 Mustard St. Suite 250
Rochester, NY 14609

Phone: (585) 288-5380
Fax: (585) 288-8475

July 9, 2004

Approved by:

Laboratory Manager: Mike Perry

Quality Assurance Program Manager: Lisa Reyes

Annual review of this QAM has been performed and the QAM still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

NON-CONTROLLED COPY
Will Not Be Updated

laboratory has been reviewed and approved by the Laboratory Director, the Quality Assurance Program Manager and in most cases, the appropriate laboratory supervisor. The document control process associated with an SOP ensures that only the most currently prepared version of an SOP is being used for guidance and instruction. In addition to SOPs, each laboratory supervisor maintains a current file of all the promulgated methodology used to perform analyses. This file is accessible to all laboratory staff regardless of discipline. Laboratory notebook entries have been standardized following the guidelines in the *Making Entries into Logbooks and onto Benchsheets* SOP (SOP No. ADM-DATANTRY). The entries made into laboratory notebooks are reviewed and approved by the appropriate supervisor at a regular interval (e.g. weekly, monthly, etc...)

4.2.3 Standard Reference Materials

All analytical measurements generated at CAS are performed using materials and/or processes that are traceable to a Standard Reference Material (SRM). Metrology equipment (analytical balances, thermometers, etc...) is calibrated using SRMs traceable to the National Institute of Standards and Technology (NIST). Consumable SRMs routinely purchased by the laboratories (e.g. primary stock standards) are purchased from nationally-recognized, reputable vendors. Most vendors have fulfilled the requirements for ISO 9001 certification and/or are accredited by A_2LA. Traceability throughout the laboratory is accomplished by following the guidelines set in the SOP, *Making Entries Into Logbooks and Onto Benchsheets* (ADM-DATANTRY).

All sampling containers provided to the client by the laboratory are purchased as precleaned (Level 1) containers, with certificates of analysis available for each bottle type. Certifications of Analysis provided by the vendors of reference materials and bottles are kept on file by the laboratory.

4.2.4 Operational Assessments

There are a number of methods used to assess the laboratory and its daily operations. In addition to the routine quality control (QC) measurements used by a laboratory to measure quality, the senior laboratory management staff at CAS examine a number of other performance indicators to more accurately assess the overall ability of the laboratory to successfully perform analyses for its clients. On-time performance, Analytical Report defect rate and Customer Invoice defect rate are a few of the measurements performed at CAS that are used to assess performance from an external perspective (i.e. client satisfaction). A frequent, routine assessment must also be made of the laboratory's facilities and resources in anticipation of accepting an additional or increased workload. CAS utilizes a number of different methods to insure that adequate resources are available in anticipation of the demand for service. Regularly scheduled senior staff meetings, tracking of outstanding proposals and an accurate, current synopsis of incoming

ATTACHMENT D

LABORATORY STANDARD OPERATING PROCEDURES

ATTACHMENT D-1

COLUMBIA ANALYTICAL SERVICES, INC.
STANDARD OPERATING PROCEDURES

MET-3010A, Rev. 4	**Metals Digestion, Waters for ICP Analysis**
MET-3050Pines, Rev. 0	**Metals Digestion, Soils, Sediments, and Sludge for ICP Analysis for the Pines Indiana Site**
MET-6010BPines, Rev. 1	**Determination of Metals and Trace Elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) for Indiana Pines Site**
MET-7471APines, Rev. 0	**Determination of Mercury in Solid or Semisolid Waste by Cold Vapor Atomic Absorption Spectrometry**
MET-3020A, Rev. 3	**Metals Digestion, Waters for GFAAS Analysis**
MET-3050B, Rev. 3	**Metals Digestion, Soils, Sediments, and Sludge for ICP and GFAA Analysis**
MET-GFAA, Rev. 3	**Determination of Trace Metals by Graphite Furnace Atomic Absorption Spectrometry (GFAAS)**
MET-ICSPines, Rev. 0	**Total Sulfur for Ion Chromatography for Indiana Pines Site**
GEN-300.0 Rev. 3	**Determination of Anions Using Ion Chromatography**
GEN-300Pines, Rev. 0	**Determination of Sulfur In Soils Using Ion Chromatography After Alkaline Digestion for Indian Pines Site**
GEN-2340B, Rev. 0	**Total Hardness by Calculation**
GEN-425.1, Rev. 3	**Determination of Surfactants or Methylene Blue Active Substances (MBAS)**
GEN-350.1, Rev. 3	**Ammonia by Flow Injection Analysis**
GEN-310.1, Rev. 3	**Titrametric Determination of Total Alkalinity**
GEN-415.1/9060, Rev. 5	**Total Organic Carbon in Water**
GEN-9030B/9034, Rev. 1	**Determination of Sulfides by Distillation and Iodometric Titration**
GEN-370.1, Rev. 1	**Colorimetric Determination of Silica in Water**
GEN-160.2, Rev. 3	**Total Suspended Solids (TSS)**
MET-3050 Pines, Rev. 0	**Metals Digestion, Soils, Sediments, and Sludges for ICP Analysis for Indiana Pines Site**
GEN-TOCLK/9060, Rev. 2	**Total Organic Carbon in Soils**
ADM-MDL, Rev. 5	**The Determination of Method Detection Limits**
SMO-GEN, Rev. 2	**Sample Receiving**
GEN-opo, Rev.1	**Orthophosphate, Colorimetric Determination Using EPA 365.1**

STANDARD OPERATING PROCEDURE

for

**METALS DIGESTION,
WATERS FOR ICP ANALYSIS**

SOP No.: MET-3010A

Revision: 4

April 4, 2002

Approved by: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: ______ Date: ___________
Initials: ______ Date: ___________
Initials: ______ Date: ___________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: ___________

1. SCOPE AND APPLICATION

Method 3010A is an acid digestion procedure used to prepare aqueous samples, TCLP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by ICP or atomic absorption analysis for total metals.

2. METHOD SUMMARY

Nitric acid is added to a representative aliquot of sample and refluxed in a beaker. This step is repeated until the digestate is light in color or until the color has stabilized. After the digestate has been brought to a low volume, it is refluxed with HCl and brought to volume.

3. DEFINITIONS

3.1. **Laboratory Duplicates -** Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2. **Laboratory Control Sample (LCS)** - An aliquot of to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3. **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4. **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5. **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4. INTERFERENCES

See appropriate analytical SOP for applicable interferences

5. SAFETY

Nitric and Hydrochloric Acid are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment will include safety glass (with side shields), gloves and a lab coat.

6. SAMPLE PRESERVATION AND STORAGE

For aqueous samples, glass or plastic sample containers are acceptable. Sample volume should be acid preserved with (1+1) nitric acid to pH <2. Samples are analyzed within 6 months of sample collection. Additional sample handling, storage, and custody procedures are discussed in SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. 250 ml or 100 ml beakers
7.2. Ribbed watch glasses
7.3. Hot plates
7.4. Graduated cylinders
7.5. Eppendorf Pipettors
7.6. Hot Block digestor with ETR-3200 Controller by Environmental Express, LTD.
7.7. Graduated block digestor sample cups with screw caps or snap down caps.
7.8. Block digestor ribbed watch glasses or reflux cap.
7.9. Filter paper
7.10. Repipetor
7.11. Block Digestor Filters
7.12. Hot Block digestor – CPI MOD Block.

8. PREVENTIVE MAINTENANCE

All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9. STANDARDS AND REAGENTS

9.1. ASTM Type II water

9.2. Concentrated nitric acid (Baker Instra-Analyzed 69-70%) –purchased commercially. Store at room temperature in the dark. Expires as per manufacturer's indications or 3 years from receipt, whichever is sooner.

9.3. Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%) - purchased commercially. Store at room temperature. Expires as per manufacturer's indications or 3 years from receipt, whichever is sooner.

9.4. Metals spiking solutions- See Table 1 – expires as per manufacturer's indications or three years from receipt, whichever is sooner.

10. RESPONSIBILITIES

It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10. PROCEDURE

10.1. HOT PLATE

10.1.1. Shake the samples and measure a 50 ml aliquot using a graduated cylinder into a 250 mL or 100 ml beaker. Rinse the cylinder three times with DI water to ensure quantitative transfer of sample. All rinses should be added to the beaker for digestion. At this point use an eppendorf pipet to add the appropriate spiking solutions (Table 1) directly onto the designated spike sample prior to addition of water or other reagents.

10.1.2. Using a repipetor, add 1.5 ml of concentrated HNO_3 and 5 ml of 1:1 HCl to sample. Place beaker on hot plate and evaporate to a low volume (5 ml), making certain the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker. Using a repipetor, add another 1.5 ml portion of HNO_3, cover with a watch glass and heat so that a gentle reflux action occurs. (CAUTION: Do not allow sample to go dry. Should this occur, discard sample and reprepare.) Continue refluxing until digestion is complete. (Additional acid may be required). Digestion is complete when the digestate is light in color or when the color has stabilized

10.1.3. For ICP analyses, reduce the sample volume to 5 ml. Remove the beaker from the hot plate and allow to cool. For TCLP analyses, add 7.5 ml concentrated HCl using a repipetor and allow to cool.

10.1.4. Rinse down the sides of the beaker and the watch glass with DI water and transfer the digestate to a graduated cylinder. Dilute to a final volume of 50 mls. Pour the 50 ml digestate into a labelled B-cup. Transfer the digestate between the B-cup and graduated cylinder at least once to mix digestate. Allow digestates to settle before analysis. If immediate analysis is necessary the digestates may be filtered or centrifuged to remove insoluble material. All filters must be rinsed with 1:1 nitric acid then DI water before use.

10.2. HOT BLOCK DIGESTOR

10.2.1. Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

10.2.2. The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

10.2.3. Label graduated hot block digestor sample cups with appropriate sample ID's for digestion. Shake the sample and measure 50ml aliquot into the designated graduated hot block digestor sample cup. At this point use a calibrated eppendorf pipet to add the appropriate spiking solutions (Table 1) directly into the designated spike sample prior to addition of reagents.

10.2.4. Using a repipetor, add 3 ml of concentrated HNO_3 and 5 mL of 1:1 HCl to sample. Cover the sample with a disposable ribbed watch glass or reflux cap and place in Block Digestor at 90 to 95°C until the volume has been reduced to a low volume (5 mL).

CAUTION: Do not boil. Antimony is easily lost by volatilization.

10.2.5. Digestion is complete when the digestate is light in color or when the color has stabilized

10.2.6. For ICP analyses, reduce the sample volume to 5 mL. Remove the beaker from the hot block and allow to cool. For TCLP analyses, add 7.5 mL concentrated HCl using a repipetor and allow to cool.

10.2.7. Cool the sample and dilute sample to 50ml in the graduated hot block digestor sample cup. Cover with screw cap and mix well. Place label on screw cap.

10.2.8. Insoluble material is allowed to settle overnight, or the digestate may be centrifuged or filtered. All filters must be rinsed with 1:1 nitric acid then DI water before use.

12. QA/QC REQUIREMENTS

12.1. Monitor temperature of samples during digestion. Record in digestion log.

12.2. Each day, digest one laboratory control sample with each batch. Use the appropriate dilution of metals spike solution (see Table 1).

12.3. Digest one preparation blank per matrix. Each day, prepare one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use 50 mLs D.I. water and follow the digestion procedures.

12.4. Digest one duplicate and one spiked sample with each sample matrix. Each day, prepare one duplicate and spike sample per each digestion batch, or per twenty samples whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements. Water spikes are prepared by the appropriate volume of spiking solution (see Table 1).

12.5. See appropriate analytical SOP and Appendix C of the Quality Assurance Manual for applicable QC limits and corrective action.

13. DATA REDUCTION AND REPORTING

13.1. Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log. The temperature of the samples during digestion is recorded on the prep sheet approximately 1.5 hours into the digestion. See attached digestion log benchsheet.

13.2. Data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1. Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

15.2. Acidic waste is poured down the drain with copious amounts of water.

15.3. Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste, see SMO-SPLDIS.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods," EPA SW-846, 3rd Edition, July 1992.

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2. Observe Sample Preparation. Follow Training Plan Form.

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Perform an Initial Demonstration of Capability (IDC) by performing the analysis independently and analyzing a known standard four times. Recovery must be within acceptable limits. Complete summary spreadsheet, IDC certification form and Training Plan Form and file forms with QA.

19.5. Continuing capability shall be demonstrated annually using an outside PE source, an LCS, an internal unknown, or a new 4 replicate study.

20. METHOD MODIFICATIONS

HCl is added at the beginning of preparation rather than the end to avoid loss of Sb and Ag (10.2.4)

21. INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

22. ATTACHMENTS

- Table 1 Spike Concentrations for LCS and MS Samples
- SW846 Method 3010A Flow Chart
- Digestion Log Benchsheet

23. CHANGES FROM PREVIOUS REVISION

- Changed 11.2.1 to be less specific about what temperature to set the digestor and more focused on the temperature of the samples
- Added need to monitor samples during digestion and record on prep sheet (13.1 and 12.1)
- Changed attachment of digestion log benchsheet to include ILM 4.1
- Added storage and expiration to reagents (9)
- Added Sections 14, 16, 17, and 20 for NELAP compliance
- Added references to ADM-TRANDOC and the Training Plan Form to the Training Section (19)
- Referenced Appendix C of the Quality Assurance Manual in QA/QC (12)

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A		0.500ml Spk A	to Final Volume of 50mL
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
AL	200	**NI**	50
AS	4	**SE**	1
BA	200	**AG**	5
BE	5	**TL**	200
CD	5	**V**	50
CR	20	**ZN**	50
CO	50	**B**	100
CU	25	**CA**	200
FE	100	**MG**	200
PB	50	**NA**	2000
MN	50	**K**	2000

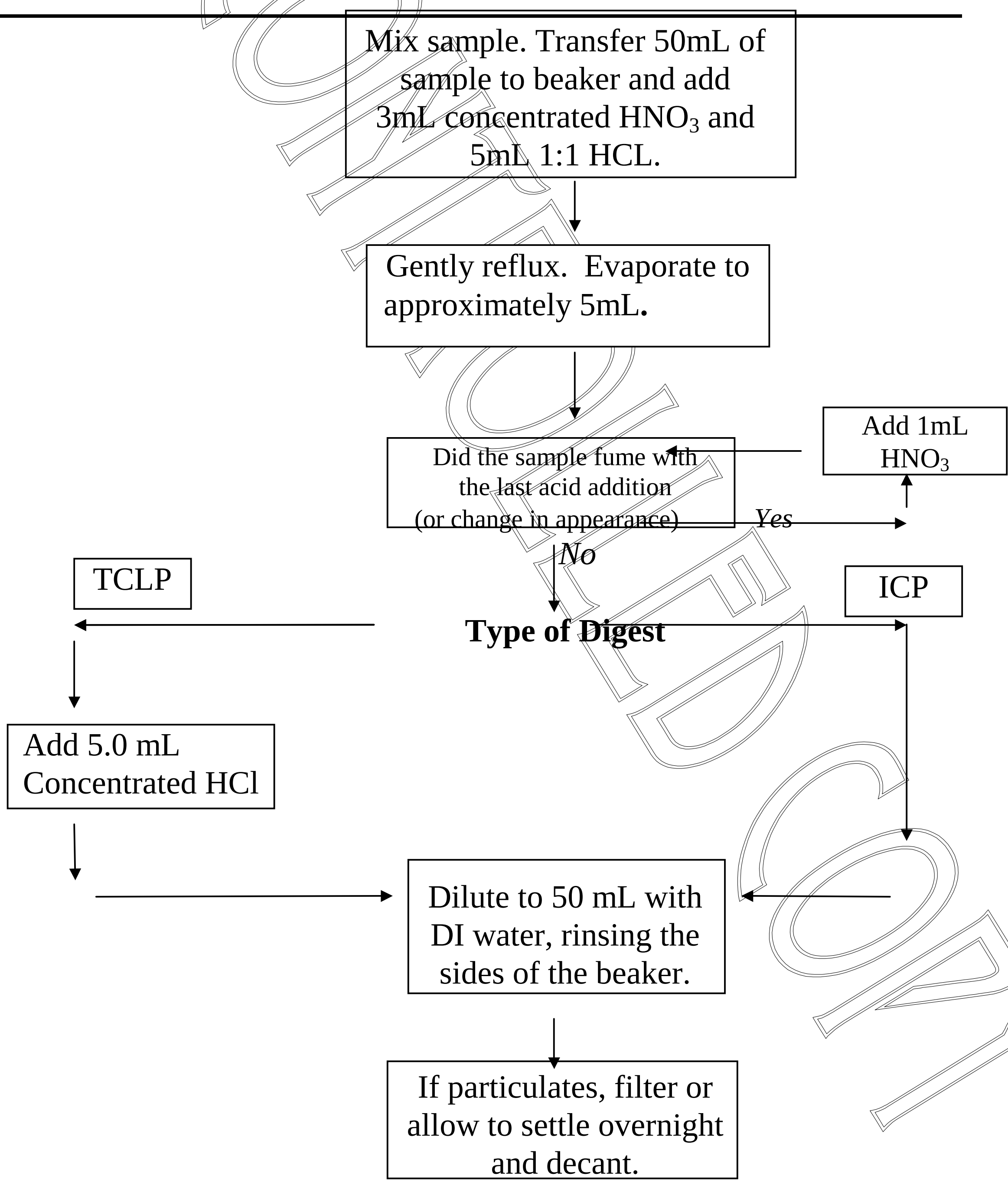
SPIKE SOLUTION B		0.500ml Spk B	to Final Volume of 50mL
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
SB	50	**TI**	50
MO	50	**-**	-

INDIVIDUAL METALS	0.050mL Spk. to Final Volume of 50mL	**INDIVIDUAL METALS**	0.25mL Spk. to Final Volume of 50mL
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
SE	1000	**SN**	1000

SPIKE #4 Furnace Spike		0.500ml Spk #4	to Final Volume of 50mL
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
AS	4	**SB**	5
PB	2	**TL**	5
SE	1	**-**	-

SW846 Method 3010A
Flow Chart

Dirty Routine Water and TCLP Digestions



SC

CAS-Rochester ICP Water Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: ____________ Date: ________ Spk Witness: __________

Prep Method: 3010 // 3010 TCLP // 3005 // CLP

Report Type: Routine // ASP // Pkg5

Digest: Initial // Redigest of: ____________

Approval: __________

	Submission / Order #	pH	Initial Vol (ml)	Final Vol (ml)	Initial Color / Clarity	Final Color / Clarity	Metals	Spike Vol (ml)
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								

Spiking Standards / Reagent Lot #:

Spike A,B: ____________ Spike #4: ____________

TCLP Spk: ____________ TCLP Ba: ____________

Se Std: ____________ Sn Std: ____________

HNO3: ____________ HCL: ____________

Color / Clarity Key:

Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown

BL = Black ; **G** = Grey

Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque

Comments: ______________________________

STANDARD OPERATING PROCEDURE

for

**METALS DIGESTION,
SOILS, SEDIMENTS, AND SLUDGE FOR ICP ANALYSIS
FOR INDIANA PINES SITE**

SOP No.: MET-3050pines

Revision: 0

September 28, 2004

Approved by: Christine Kutzer 9/28/04
Supervisor Date

Lisa Reyes 9/28/04
QA Coordinator Date

Michael K. Perry 9/28/04
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _______ Date: ___________
Initials: _______ Date: ___________
Initials: _______ Date: ___________

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1 SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 3050B for the digestion of soils, sludges, or sediments for analysis by ICP. As stated in the EPA method, "this method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment." This SOP was written specifically for the Indiana Pines Site.

2 SUMMARY OF METHOD

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS)** - An aliquot of a soil to which known quantities of the method analytes are added. The LCSS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 HEALTH AND SAFETY WARNINGS

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

5 CAUTIONS

Antimony is easily lost by volatilization. Do not boil the digestate.

6 INTERFERENCES

Use more sample for those samples with high moisture content to meet detection limits.

7 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8 EQUIPMENT AND SUPPLIES

8.1 Eppendorf Pipettors
8.2 Funnels
8.3 Mortar and pestle
8.4 Tongue depressors
8.5 Filter paper
8.6 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
8.7 Graduated block digestor cups
8.8 Block Digestor Filters.
8.9 CPI MOD Block Digestor

8.10 Reagent water - ASTM Type II deionized water.

8.11 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Store at room temperature in the dark in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.12 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Store at room temperature in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.13 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the original container. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.14 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.15 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expire upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

9 PROCEDURES

9.1 Sample Collection – Collect samples in purchased, certified clean glass or plastic.

9.2 Sample Handling and Preservation – Analyze samples within 6 months of sample collection. Store samples in a refrigerator or at room temperature. Sample receiving, handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

9.3 Sample Preparation

9.3.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

9.3.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

9.3.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

9.3.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

9.3.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

9.3.6 Unless otherwise specified by project requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

9.3.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

9.3.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

9.3.9 Add 10 mL 1:1 HCL.

9.3.10 Cover and reflux the samples for 15 minutes without boiling. Allow to cool.

9.3.11 Rinse filters with 1:1 nitric acid and DI.

9.3.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

9.4 **Sample Analysis** – Give digested samples and a copy of the prep sheet to the ICP analyst. Analyze according to MET-6010Bpines.

9.5 **Troubleshooting -** All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9.6 **Data Acquisition, Calculations and Data Reduction Requirements**

Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

10 DATA AND RECORDS MANAGEMENT

10.1 Responsibilities - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2 Data will be reviewed after ICP analysis according to MET-6010Bpines.

11 QA/QC REQUIREMENTS

11.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

11.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

11.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

11.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

11.5 See MET-6010Bpines for applicable QC limits and corrective action.

12 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

NELAC, 2002 Standard.

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AL	200		**NI**	50
AS	4		**SE**	1
BA	200		**AG**	5
BE	5		**TL**	200
CD	5		**V**	50
CR	20		**ZN**	50
CO	50		**B**	100
CU	25		**CA**	200
FE	100		**MG**	200
PB	50		**NA**	2000
MN	50		**K**	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SB	50		**TI**	50
MO	50		-	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		**INDIVIDUAL METALS**	0.5ml Spk. to Final Volume of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SE	1000		**SN**	1000

CAS-Rochester ICP Soil Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID: ____

Analyst: ____________ **Date:** ______

Spike Witness / Lot Approval: ____________

Batch Temp: ____

Prep Method: SW846 3050 // CLP

Digest: Initial // Redigest of: ____________

Report Type: Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: ____________ Spike #4: ____________
TCLP Spk: ____________ TCLP Ba: ____________
Se Std: ____________ Sn Std: ____________
HNO3: ____________ HCL: ____________
H2O2: ____________ LCSS: ____________

Color / Clarity Key:

Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown
BL = Black ; **G** = Grey ; **W** = White
Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque
Texture: **F** = Fine ; **M** = Medium ; **CS** = Coarse ; **NAQ** = Non Aqueous

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Comments: ____

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF METALS AND TRACE ELEMENTS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP) FOR INDIANA PINES SITE

SOP No.: MET-6010BPINES

Revision: 1

September 29, 2004

Approved by: ______________________ Department Supervisor 9/29/04 Date

______________________ Laboratory Manager 9/29/04 Date

______________________ QA Coordinator 9/29/04 Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _______ Date: ____________
Initials: _______ Date: ____________
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1. SCOPE AND APPLICABILITY

1.1. This SOP uses EPA SW-846 Method 6010B for the determination of trace elements, including metals, in solution using Inductively coupled plasma-atomic emission spectrometry (ICP-AES). The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. The Method Reporting Limits (MRL) are listed in Table 1. The reported MRL may be adjusted if required for specific project requirements, however, the capability of achieving other reported MRLs must be demonstrated. Results may be reported to the Instrument Detection Limits (IDLs) upon request.

1.3. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

2.1. Samples are digested according to one of the proper metals digestion methods listed in SW-846.

2.2. This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences (discussed later) should also be recognized and appropriate corrections made.

3. DEFINITIONS

3.1. Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.2. Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration

3.3. Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45 μm membrane filter assembly prior to sample acidification.

3.4. Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength.

3.5. Initial/Continuing Calibration Verification Solution (ICV/CCV) - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6. Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component

3.7. Laboratory Duplicates - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.8. Laboratory Control Sample (LCS) - An aliquot of to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.9. Matrix Spike - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.10. Preparation Blank (PB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.11. Linear Range - The concentration range over which the instrument response to an analyte is linear.

3.12. Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.13. Plasma Solution - A solution that is used to determine the optimum height above the work coil for viewing the plasma.

3.14. Interference Check Solution (ICS) - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria.

3.15. Method Reporting Limit Standard (MRL) – Standard prepared with a known concentration of elements to check accuracy at the low end of the curve.

3.16. HLCCV1 – A standard prepared at the bench at a high concentration to encompass the range of the samples being analyzed. This standard is used to assess accuracy at the high end of the linear range.

3.17. HLCCV2 – A standard prepared slightly higher than the calibration range for metals.

3.18. Batch – a group of no more than 20 field samples digested or analyzed together on the same day with the same reagents.

4. HEALTH AND SAFETY WARNINGS

4.1. Corrosives - Because all samples and standards are diluted in 2% HNO_3 and 5% HCl, there is a danger of exposure to corrosives, sufficient care must be taken in handling these solutions. Safety glasses must be worn while preparing and handling the solutions.

4.2. High Voltage - The power unit supplies high voltage to the RF generator which is used to form the plasma. The unit should never be opened. Exposure to high voltage can cause injury or death.

4.3. UV Light - The plasma when lit is a very intense light, and must not be viewed with the naked eye. Protective lenses are in place on the instrument. Glasses with special protective lenses are available.

4.4. When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood

5. INTERFERENCES

There are several types of interferences by the ICP's: Spectral interferences can be from an overlap of spectral lines, background points or background from line emissions of high concentration elements. Physical interferences are effects associated with the sample introduction process, example high dissolved solids buildup on the nebulizer tip. Chemical interferences caused by the sample matrix itself. IEC's aid in eliminating some of these interferences. IECs are interelement correction factors that the instrument uses to compensate for spectral overlap when analyzing samples with complex spectra. Refer to Method 6010B Section 3.0 or Method 200.7 Section 4.0 for more detail and suggested procedures to correct and adjust the instrument due to interferences.

6. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7. EQUIPMENT AND SUPPLIES

7.1. ICP- Perkin Elmer Optima 3000XL - Inductively coupled argon plasma emission spectrometer (ICP) equipped with the following:

7.1.1. Computer-controlled emission spectrometer with background correction.

7.1.2. Mass flow controller for argon nebulizer gas supply.

7.1.3. Peristaltic pump.

7.1.4. Autosampler.

7.1.5. Argon gas supply - high purity.

7.2. Volumetric flasks, class A .

7.3. Trace metals grade chemicals shall be used in all tests.

7.3.1. Hydrochloric acid (conc), HCl. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.2. Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.3.3. Nitric acid (conc), HNO_3. Purchased commercially. Store at room temperature. Expires three years from receipt or upon manufacturer's indications, whichever is sooner.

7.3.4. Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriately sized beaker. Store at room temperature. Expires one year from preparation.

7.4. Reagent Water. All references to water in the method refer to DI Type II water unless otherwise specified. Reagent water will be interference free.

7.5. All standards are prepared from NIST traceable stock standard solutions. Manufacturers expiration dates are used to determine viability of standards. Preparatory procedures for standards and QC solutions vary between instruments due to the working ranges. All preparatory information for the QA/QC samples are provided in Appendix I.

7.5.1. Mixed Calibration Standards are prepared by combining appropriate volumes of the stock solutions in volumetric flasks. Matrix match with the appropriate acid and dilute to 100ml with water. Calibration standards should be verified using a second source quality control sample (LCS, ICV, or CCV). Calibration standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 7 days.

7.5.2. Initial and Continuing Calibration Verification (ICV and CCV) Standards are prepared by combining compatible analytes at concentrations equivalent to the midpoint of their respective calibration curves. The ICV and CCV standards should be prepared from a separate source independent from that used in the calibration standards. ICV / CCV standards should be stored at room temperature in glass volumetric flasks with a shelf-life of 48 hours.

7.5.3. MRL Standards are prepared to contain known concentrations of elements at or near the Method Reporting Limit. MRL standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.4. Interference Check Solutions A and AB are prepared to contain known concentrations of interfering analytes that will provide an adequate test of the correction factors. ICSA / ICSAB standards should be stored in plastic containers with a shelf-life of 6 months.

7.5.5. Laboratory Control Sample and Matrix Spike are purchased as custom mixes stored in plastic containers with a shelf-life of 6 months at the concentrations recommended in the method. Certificates of analysis are attached in Appendix I. Each sample, up to 100 mL, is spiked with 1.0 ml of spike solution.

7.6. Blanks

7.6.1. Method Blanks must contain all the reagents and in the same volumes as used in the preparation of samples. The method blanks must be carried through the complete procedure and contain the same acid concentration in the final solution as the samples.

7.6.2. The Calibration Blank is prepared by acidifying reagent water to the same concentrations of acid found in the standards and samples.

7.7. Reagent Receiving Log

The manufacturer, lot number, standard /reagent name, concentration, date received and expiration date are recorded in a reagent log.

8. PROCEDURE

8.1. Calibration and Standardization

Calibration is accomplished daily using 3 calibration standards and a blank for each element using the internal standard technique. See Sample Analysis section for more information.

8.2. Sample Collection

Containers may be glass or plastic. Samples are cooled with ice to be shipped to the laboratory.

8.3. Sample Handling and Preservation

8.3.1. Solid samples require no preservation prior to analysis other than storage at 0-6°C. Samples are analyzed within 6 months of collection.

8.3.2. Aqueous samples are acid preserved with (1+1) nitric acid to pH <2. Samples are analyzed within 6 months of sample collection.

8.3.3. Samples are checked upon receipt for all the elements listed in the Sample Acceptance Policy found in NELAC 2002 Standard.

8.3.4. For the determination of the dissolved elements, filter the sample through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a well ventilated area or fume hood.

8.3.5. Samples received by the ICP lab as digestates contain nitric and hydrochloric acid. Digestates are stored at room temperature in plastic B-cups.

8.3.6. Following analysis, digestates are stored until all results have been reviewed. Digestates are diluted and disposed of through the sewer system in approximately 90 days after receipt of sample.

8.4. Sample Preparation

8.4.1. Digest samples prior to analysis. Refer to the following Metals Methods found in SW-846:

- 3005A Metals Digestion, Waters, Total Recoverable and Dissolved for ICP
- 3010A Metals Digestion, Waters for ICP
- 3020A Metals Digestion, Waters for GFAA
- 3050B Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA

8.5. Sample Analysis

8.5.1. Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 45 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided in Table 3.

8.5.2. Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data documents the selection criteria of background correction points; linear ranges, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

8.5.3. Turn on power supply for the instrument, computer, printer and light the plasma. Allow instrument to warm-up for 45-60 minutes before operation. The cooling water and the argon are on when the instrument are on.

8.5.4. Profile the instrument on a daily basis, and when maintenance is done to align it optically for both horizontal and vertical optimization in either mode. Aspirate a 10 ppm source of manganese (as recommended by the manufacturer). Choose the Tools menu/Spectrometer Control/Optimize X&Y. The instrument automatically adjusts the torch viewing position for maximum intensity.

8.5.5. Pour the 3 calibration standards, ICV/CCV standards, MRL, ICSA, and ICSAB up to 40 mL in 50 mL centrifuge tubes and add 0.80 mL of the internal standard solution. Pour all other samples, preparation blanks and laboratory control samples up to 10 mL in 15 mL centrifuge tubes and add 0.20 mL of internal standard solution. This gives an apparent concentration of 1.00 mg/L Yttrium. The Yttrium intensity is used by the instrument to ratio the analyte intensity signals for both calibration and quantitation. Cesium is used only as a stabilizer.

8.5.6. Internal standards can be added via pump and mixing block. This technique uses a solution of 10 mg/L Y and 10 mg/L Cs.

8.5.7. Following the calibration, analyze in the following sequence:

- ICV; ICB; MRL; ICSA; ICSAB; CCV; CCB;
- 10 environmental samples (including PBs and LCSs); CCV; CCB; repeat to the end of the run…..
- Last 10 samples; CCV; CCB, MRL, ICSA, ICSAB; HLCCV1; HLCCV2; CCV; CCB.

8.5.8. Rinse the system with the calibration blank solution before the analysis of each sample for one minute.

8.5.9. Samples which exceed the linear range of the instrument must be diluted and reanalyzed.

8.5.10. Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit. See Table 2 for approximate wavelengths. See 40 CFR Part136 Appendix B for more information.

8.6. Troubleshooting

8.6.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument. Most routine maintenance and troubleshooting is performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Record the analytical run filename of the first acceptable run after major maintenance in the maintenance log book. Typical preventive maintenance measures include, but are not limited to, the following items:

- Cleaning the pump tubing as needed
- Empty waste container, as needed
- Cleaning the nebulizer, spray chamber, and torch, as needed
- Replace water and vacuum filters, as needed

8.7. Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1. Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported with up to three significant figures.

8.7.2. Sample Calculation (water)

$$\text{Conc. (mg/L)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial volume (L)}}$$

8.7.3. Sample Calculation (soils)

$$\text{Conc. (mg/g)} = \frac{\text{Instrument Reading (mg/L) x Final digestion volume (L)}}{\text{Initial mass (g) x Percent Solids expressed as a decimal}}$$

8.7.4. **Matrix Spike Recovery** is calculated to determine accuracy for matrix and blank spikes using the following equation:

$$\text{Accuracy (\%REC)} = \frac{A - B}{C} \times 100$$

Where
A = Analyte total concentration from spiked sample
B = Analyte concentration from unspiked sample
C = Concentration of spike added

8.7.5. **Precision** is measured through the use of replicate sample analyses within the same batch and is expressed as the relative percent difference (RPD) between the replicate measurements.

$$\text{RPD} = \frac{|D1 - D2|}{(D1+D2)/2} \times 100$$

Where
D1 = Original Result
D2 = Duplicate Result

Report each analyte concentration to the proper significant figures in mg/L or µg/L as required.

8.8. Computer Hardware and Software

Each ICP uses a Gateway GP5-233 running the ICP WinLab v.1.42.
Metals Analytical Review and Reporting System (MARRS) v.3.2.44
StarLIMS v.6.11.a

9. DATA AND RECORDS MANAGEMENT

9.1. **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using ICP software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

9.3. Data Review - Data will be reviewed by the ICP analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10. QUALITY CONTROL AND QUALITY ASSURANCE

10.1. Instrument values are based on duplicate readings. Precision between the emission readings shall not exceed 20 %RSD. If RSD values exceed 20%, the sample reanalyzed and reported.

10.2. Preparation Blanks must be analyzed at least one PB with each batch of 20 or fewer samples of the same matrix. PB values must not exceed the MRL. Fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained. If detections are greater than the MRL, the batch needs to be redigested if sample concentration is less than 5 times the concentration found in the prep blank. If the sample concentration is less than the MRL the sample does not require redigestion.

10.3. HLCCV1 – High standard used in curve and analyzed once during daily analysis. Should agree within 10% of the true value. If HLCCV1 is > 10% different the analysis is judged to be out of control and the source of the problem should be identified and resolved before continuing analysis.

10.4. HLCCV2 – standard slightly higher than calibration for some metals. Analyzed once during daily analysis. Should agree within 10% of the true value. If out of control, client data above the HLCCV1 should be re-analyzed.

10.5. ICV/CCV - Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within 10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of an analyte falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Recalibrate the instrument.

10.6. The results of the calibration blank (CCB) must be less than the MRL. If not, terminate the analysis, correct the problem, recalibrate, and reanalyze the samples effected.

10.7. Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

10.8. Analyze matrix spiked and duplicate samples at a frequency of one per matrix batch (max. 20 samples). Matrix spiked and duplicate samples are brought through the entire sample preparation and analytical process.

10.8.1. The spiked sample or spiked duplicate sample recovery is to be within ± 25% of the actual value or within the documented historical acceptance limits for each matrix. Sample concentrations greater than four times the spike concentration are not valid and shall not be evaluated. If the matrix spike does not meet these criteria, analyze a Post Digestion Spike.

10.8.2. A control limit of ± 20% RPD shall be used for original and duplicate samples greater than or equal to 5X the CRDL. A control limit of ± the CRDL shall be used if either the sample or duplicate value is less than 5 times the CRDL. CRDL values are given in Table 1.

10.9. Laboratory Control Sample – verify sample preparation and analysis using reagent water spiked with a known amount of analytes of interest. Results should be within ± 20%. Outlying recoveries may indicate loss of analyte due to digestion procedures or laboratory contamination. If an LCS is found to be out of the specified limits, recalibrate and reanalyze. If the LCS remains out of the specified limits, redigestion of the entire batch should occur if the recovery is less than 80%. If the LCS recovery is greater than 120% redigest all positive results (greater than the MRL).

10.10. MRL standard- A standard at or near the MRL is analyzed at the beginning and end of each analytical run but not before the ICV. There are no limits in the 6010B method, but the CAS guideline used is +/- 50% of the true value. If the limits are not met the analysis is stopped and the instrument is recalibrated.

10.11. Interference Check Samples- The ICSA and ICSAB need to be run consecutively at the beginning and end of each analytical run. Results from the ICSA solution shall be monitored for false positive detections of analytes not present in the mix. The analyte recoveries for the AB solution must fall within 20% of the true value otherwise the run must be stopped, recalibrated and reanalyzed unless analytes are not detected in the associated samples or interferent elements are not present.

10.12. Serial Dilution Test If the analyte concentration is sufficiently high (minimally, a factor of 50 times above the IDL), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected and data may be flagged accordingly.

10.13. Post Digestion Spike Addition: Typically if a matrix spike does not yield acceptable results, a post-digestion spike may be added to a portion of a prepared sample, or its dilution, and should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the IDL. If the spike is not recovered within the specified limits, a matrix effect has been confirmed.

10.14. Instrument Performance

- InterElement Correction Factors (IEC) are analyzed annually, or as needed.
- Linear Ranges (LR) are run biannually and must be ±5% of true value.
- Instrument Detection Limits (IDL) are analyzed quarterly, or as needed.
- Method Detection Limits (MDL) are analyzed annually.

11. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods.* USEPA SW-846, 3rd Edition, December 1996.
- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994.
- 40 CFR Part136 Appendix B
- NELAC 2002 Standard

Metals Instrument Analysis Training Plan

Procedure:____

SOP:________________ Revision:__________ Date:________

Trainee:______________________

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
-the chemical and physical principals behind the measurement by the instrument

Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
-standard and reagent prep and documentation – including pipet used
-instrument power up and warm-up
-instrument set-up, daily maintenance and checks
-use and loading of autosampler
-sample analysis including:
    -calibration
    -sample dilution
    -software command of instrument
    -use of QC samples and QC criteria
    -common troubleshooting
-instrument logbook use
-data reduction, reporting, and review

Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

Signature:__________________________ Date:__________

6. Perform SOP with supervision
- including all items in 4.

Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
-all of the item listed in 4
-IDC (4 mid-range standards performed before client samples are analyzed)
-attach IDC certificate, raw data, and summary spreadsheet.

Trainer:____ Trainee:____ Date:____

TABLE 1

Analyte	*MRL* ***Water*** ***mg/L***	***MRL*** ***Soil*** ***ug/g***	*Typical IDL* ***ug/L***
Silver	0.010	1.00	0.632
Aluminum	0.100	10.0	6.57
Arsenic	0.0100	50.0	6.89
Boron	0.200	20.0	37.3
Barium	0.0200	2.00	12.2
Beryllium	0.0050	0.500	0.26
Calcium	0.500	50.0	167
Cadmium	0.0050	0.500	0.489
Cobalt	0.0500	5.00	3.03
Chromium	0.0100	1.0	1.81
Copper	0.0200	2.00	3.02
Iron	0.100	5.00	44.1
Potassium	2.00	100	857
Lithium	0.200	20.0	23.9
Magnesium	0.500	50.0	124
Manganese	0.0100	1.0	1.78
Molybdenum	0.0250	2.50	3.08
Sodium	0.500	50.0	193
Nickel	0.0400	4.00	3.92
Lead	0.00500	5.00	1.29
Antimony	0.0600	10.0	3.72
Selenium	0.00500	50.0	12.5
Silicon	1.00	100	68.7
Strontium	0.100	10.0	5.38
Tin	0.500	100	15.8
Titanium	0.0500	5.00	3.15
Thallium	0.0100	30.0	7.77
Vanadium	0.0500	5.00	2.74
Zinc	0.0200	1.0	2.47

Table 2

Recommended Wavelengths and Instrument Specifications

Suggested wavelengths are listed below:

Analyte	Wavelength
Ag Silver	328.068
Al Aluminum	308.215
B Boron	249.773
Ba Barium	233.527
Be Beryllium	234.861
Ca Calcium	430.253
Cd Cadmium	226.502
Co Cobalt	228.616
Cr Chromium	267.716
Cu Copper	324.754
Fe Iron	238.863
Li Lithium	610.364
Mg Magnisium	279.079
Mn Manganese	257.610
Mo Molybdenum	202.030
Na Sodium	330.237
Ni Nickel	231.604
Pb Lead	220.353
Sb Antimony	206.833
Si Silicon	252.851
Sn Tin	189.933
Sr Strontium	421.552
Ti Titanium	334.941
V Vanadium	292.402
Zn Zinc	206.191
Y Yittrium	371.030

Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions cannot be provided. The instrument operating conditions herein are recommended based upon manufacturer's instrument manuals.

Table 3
Operating Conditions

Current Method Operating Conditions are as follows, these conditions may vary to optimize the instrument for different analyses:

Parameter	Radial Plasma	Axial Plasma
Resolution	Fixed	Fixed
Purge Gas Flow	Normal	Normal
Read Time (min/max sec.)	5/20	5/50
Replicates	2	2
Plasma (L/min)	15	15
Aux. (L/min)	0.5	0.3
Nebulizer Flow (L/min)	0.72	0.56
Power (watts)	1300	1450
Viewing Height (mm)	15	15

APPENDIX I

PREPARATION PROCEDURES FOR STANDARDS AND QC

RADIAL OPTIMA #1 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			0.0050			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
PQL Std 2	B		200	0.100		0.200			W				
	MO		25			0.0250			X				
	SN		500			0.500			Y				
	TI		50			0.0500			Z				
Single std	PB	1/10-	100	0.050		0.055			AA				
	AS		1000	0.010		0.110			BB				
	SE		1000	0.010		0.105			CC				
	TL		1000	0.010		0.110			DD				
	SR		1000	0.010		0.100			EE				

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RADIAL OPTIMA #1- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	4.00	200	100	2%HNO3		A				
	MG		5000			100	5%HCl		B				
	K		5000			100			C				
	NA		5000			100			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	8.00		4.00			Q				
	CD		50			2.00			R				
	PB		50			2.00			S				
	SE		50			2.00			T				
	TL		100			4.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				
	SR		1000	1.00		5.00			AA				

RADIAL OPTIMA #1 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3		A			
	MG		5000			50.0	5%HCl		B			
	K		5000			50.0			C			
	NA		5000			50.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	4.00		2.00			Q			
	CD		50			1.00			R			
	PB		50			1.00			S			
	SE		50			1.00			T			
	TL		100			2.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			
	SR		1000	0.500		2.50			AA			

RADIAL OPTIMA #1 - HLCCV2 (Standard is prepared weekly or as necessary.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3
	CR		100			2.00	5%HCl
	MN		150			3.00	
	NI		400			8.00	
	ZN		200			4.00	
Cal Std 3	AL		2000	2.00		40.0	
	BA		2000			40.0	
	BE		50			1.00	
	CO		500			10.0	
	CU		250			5.00	
	FE		1000			20.0	
	V		500			10.0	
Single Metals	MO		1000	1.00		10.0	
	PB		1000	~~0.800~~ 1.00		10.0	
	TI		1000	1.00		10.0	

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Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
	A				
	B				
	C				
	D				
	E				
	F				
	G				
	H				
	I				
	J				
	K				
	L				
	M				
	N				
	O				
	P				
	Q				
	R				
	S				
	T				
	U				
	V				
	W				
	X				
	Y				
	Z				

RADIAL OPTIMA #1 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			BELOW			C				
BE		10			0.0100			D				
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			BELOW			K				
SB		120			0.120			L				
SE		10			BELOW			M				
TL		20			BELOW			N				
V		100			0.100			O				
ZN		40			0.0400			P				
AS		1000	0.050		0.120			Q				
PB		1000	0.050		0.106			R				
SE		1000	0.050		0.110			S				
TL		1000	0.050		0.120			T				

RADIAL OPTIMA #1 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		100			1.00			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		100			1.00			P				
V		50			0.500			Q				
ZN		100			1.00			R				
								S				
								T				
								U				

RADIAL OPTIMA #1 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal	Ca		5000	0.20	1000	1.00	5% HCL		A				
#1	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal	Cr		100	0.10		0.0100			E				
#2	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal	Al		2000	0.10		0.200			J				
#3	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal	Cd		50	0.10		0.0050			Q				
#4	As , Tl		100			BELOW			R				
	Pb , Se		50			BELOW			S				
PQL	B		200	1.00		0.200			T				
#2	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Ti		50			0.050			W				
Single	Sb		1000	0.060		0.060			X				
Stds	Sr		1000	0.100		0.100			Y				
	Tl		1000	0.300		0.310			Z				
	As		1000	0.500		0.510							
	Se		1000	0.500		0.505							
	Pb		1000	0.050		0.055							

AXIAL OPTIMA #2 CALIBRATION STANDARD #1 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
PQL Std 1	AL		200	0.100	100	0.200	2%HNO3		A				
	BE		5			0.0050	5%HCl		B				
	CO		50			0.0500			C				
	MG		5000			5.00			D				
	SE		5			BELOW			E				
	V		50			0.0500			F				
	SB		60			0.0600			G				
	CD		5			BELOW			H				
	CU		25			0.0250			I				
	MN		15			0.0150			J				
	AG		10			0.0100			K				
	ZN		20			0.0200			L				
	AS		10			BELOW			M				
	CA		5000			5.00			N				
	FE		100			0.100			O				
	NI		40			0.0400			P				
	NA		5000			5.00			Q				
	BA		200			0.200			R				
	CR		10			0.0100			S				
	PB		5			BELOW			T				
	K		5000			5.00			U				
	TL		10			BELOW			V				
Cal Std 4	AS		100	0.010		0.0200			W				
	CD		50			0.0100			X				
	SE		50			0.0100			Y				
	PB		50			0.0100			Z				
	TL		100			0.0200			AA				
PQL Std 2	B		200	0.100		0.200			BB				
	MO		25			0.0250			CC				
	SN		500			0.500			DD				
	TI		50			0.0500			EE				07

AXIAL OPTIMA #2- CALIBRATION STANDARD #3 / HLCCV1 (Standard is prepared weekly or as necessary)
(CALIBRATION STANDARD #2 IS A 1/5 DILUTION OF THIS STANDARD)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 1	CA		5000	2.00	200	50.0	2%HNO3		A				
	MG		5000			50.0	5%HCl		B				
	K		5000			50.0			C				
	NA		5000			50.0			D				
Cal Std 2	AG		100	2.00		1.00			E				
	CR		100			1.00			F				
	MN		150			1.50			G				
	NI		400			4.00			H				
	ZN		200			2.00			I				
Cal Std 3	AL		2000	2.00		20.0			J				
	BA		2000			20.0			K				
	BE		50			0.500			L				
	CO		500			5.00			M				
	CU		250			2.50			N				
	FE		1000			10.0			O				
	V		500			5.00			P				
Cal Std 4	AS		100	4.00		2.00			Q				
	CD		50			1.00			R				
	PB		50			1.00			S				
	SE		50			1.00			T				
	TL		100			2.00			U				
Single Metals	SB		1000	2.00		10.0			V				
	SN		1000	2.00		10.0			W				
	B		1000	1.00		5.00			X				
	MO		1000	1.00		5.00			Y				
	TI		1000	1.00		5.00			Z				

AXIAL OPTIMA #2 ICV/CCV STANDARD (Standard is prepared daily.)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Pipet ID
Cal Std 1	CA		5000	1.00	200	25.0	2%HNO3		A			
	MG		5000			25.0	5%HCl		B			
	K		5000			25.0			C			
	NA		5000			25.0			D			
Cal Std 2	AG		100	1.00		0.500			E			
	CR		100			0.500			F			
	MN		150			0.750			G			
	NI		400			2.00			H			
	ZN		200			1.00			I			
Cal Std 3	AL		2000	1.00		10.0			J			
	BA		2000			10.0			K			
	BE		50			0.250			L			
	CO		500			2.50			M			
	CU		250			1.25			N			
	FE		1000			5.00			O			
	V		500			2.50			P			
Cal Std 4	AS		100	2.00		1.00			Q			
	CD		50			0.500			R			
	PB		50			0.500			S			
	SE		50			0.500			T			
	TL		100			1.00			U			
Single Elements	SB		1000	1.00		5.00			V			
	SN		1000	1.00		5.00			W			
	B		1000	0.500		2.50			X			
	MO		1000	0.500		2.50			Y			
	TI		1000	0.500		2.50			Z			

AXIAL OPTIMA #2- HLCCV2 (Standard is prepared weekly or as necessary)

	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Cal Std 2	AG		100	2.00	100	2.00	2%HNO3		A				
	CR		100			2.00	5%HCl		B				
	MN		150			3.00			C				
	NI		400			8.00			D				
	ZN		200			4.00			E				
Cal Std 3	AL		2000	2.00		40.0			F				
	BA		2000			40.0			G				
	BE		50			1.00			H				
	CO		500			10.0			I				
	CU		250			5.00			J				
	FE		1000			20.0			K				
	V		500			10.0			L				
Cal Std 4	AS		100	4.00		4.00			M				
	CD		50			2.00			N				
	PB		50			below			O				
	SE		50			2.00			P				
	TL		100			4.00			Q				
Single	MO		1000	1.00		10.0			R				
Metals	PB		1000	0.800		10.0			S				
									T				
									U				
									V				
									W				
									X				
									Y				
									Z				

AXIAL OPTIMA #2 CRI STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
CRDL STD		Multi	0.500	500	Multi	5% HCL 2%HNO3		A				
AG		20			0.0200			B				
AS		20			0.0200			C				
BE		10			0.0100			D				
CD		10			0.0100			E				
CR		20			0.0200			F				
CO		100			0.100			G				
CU		50			0.0500			H				
MN		30			0.0300			I				
NI		80			0.0800			J				
PB		6			0.00600			K				
SB		120			0.120			L				
SE		10			0.0100			M				
TL		20			0.0200			N				
V		100			0.100			O				
ZN		40			0.0400			P				
								Q				

ICSA STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi	5% HCL		A				
AL		5000			500	2%HNO3		B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				
								T				
								U				
								V				

AXIAL OPTIMA #2 ICSAB STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiration Date	Pipet ID
Int. A Sol'n		Multi	100	1000	Multi			A				
AL		5000			500			B				
CA		5000			500			C				
FE		2000			200			D				
MG		5000			500			E				
Int. B Sol'n		Multi	10.0		Multi			F				
AG		20			0.200			G				
BA		50			0.500			H				
BE		50			0.500			I				
CD		100			1.00			J				
CO		50			0.500			K				
CR		50			0.500			L				
CU		50			0.500			M				
MN		50			0.500			N				
NI		100			1.00			O				
PB		5			0.0500			P				
V		50			0.500			Q				
ZN		100			1.00			R				
AS		10			0.100			S				
SB		60			0.600			T				
SE		5			0.0500			U				
TL		10			0.100			V				

OPTIMA INTERNAL STANDARD

Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Expiratio n Date	Pipet ID
Y		1000	50.0	500	100	2% HNO3		A				
Cs		1000	50.0	500	100	5% HCL		B				
								C				
								D				
								E				
								F				
								G				
								H				
								I				
								J				
								K				
								L				
								M				
								N				
								O				
								P				
								Q				
								R				
								S				

AXIAL OPTIMA #2 MRL STANDARD

	Element	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	ID Letter	Nitric Acid Lot #	Hydrochloric Acid Lot #	Exp. Date	Pipet ID
Cal #1	Ca		5000	0.20	1000	1.00	5% HCL		A				
	K		5000			1.00	2%HNO3		B				
	Mg		5000			1.00			C				
	Na		5000			1.00			D				
Cal #2	Cr		100	0.10		0.0100			E				
	Ag		100			0.0100			F				
	Mn		150			0.0150			G				
	Zn		200			0.0200			H				
	Ni		400			0.0400			I				
Cal #3	Al		2000	0.10		0.200			J				
	Ba		2000			0.200			K				
	Fe		1000			0.100			L				
	Co		500			0.050			M				
	V		500			0.050			N				
	Cu		250			0.025			O				
	Be		50			0.00500			P				
Cal #4	Cd		50	0.20		0.0100			Q				
	As , Tl		100			0.0200			R				
	Pb , Se		50			0.0100			S				
PQL #2	B		200	1.00		0.200			T				
	Mo		25			0.0250			U				
	Sn		500			0.500			V				
	Ti		50			0.050			W				
Single Stds	Sb		1000	0.060		0.060			X				
									Y				
									Z				

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MISCELLANEOUS STANDARDS

Type Of Std	Metal	CAS Lot #	Conc. (ppm)	Vol. (mls)	Final Vol. (mls)	Final Conc. (ppm)	Matrix	Analyst/ Date	Letter ID	Nitric Acid Lot#	Hydrochloric Acid Lot#	Expiration Date	Pipet ID
Cal Std1/MAL		Li:Si:Sr						SD 9/21/04	A	M17800555W	M1780054U	9/27/04	M13/M17
	Li	M1780053Y	1000	0.050	500	0.100	2% HNO_3 5% HCl	SD 9/28/04	B	M1780055W	M1780054U	10/4/04	M13/M17
	Si	M1780053X	1000	0.500		SD 9/21/04 ~~0~~1.00			C				
	Sr	M1780051N	1000	0.050		0.100			D				
									E				
Cal 3/HLCCV					200		2% HNO_3 5% HCl	SD 9/21/04	F	M1780055W	M1780054U	9/27/04	M18
	Li	M1780053Y	1000	2.00		10.0		SD 9/28/04	G	M1780055W	M1780054U	10/4/04	M18
	Si	M1780053X	1000	2.00		10.0			H				
	Sr	M1780051N	1000	1.00		5.00			I				
									J				
HLCCV2					100		2% HNO_3 5% HCl	SD 9/21/04	K	M1780055W	M1780054U	9/27/04	M18
	Li	M1780053Y	1000	2.00		20.0			L				
	Si	M1780053X	1000	2.00		20.0			M				
	Sr	M1780051N	1000	1.00		10.0			N				
									O				
ICV/CCV					200		2% HNO_3 5% HCl	SD 9/21/04	P	M1780055W	M1780054U	9/27/04	M18/M17
	Li	M1780053W	1000	1.00		5.00		SD 9/22/04	Q	M1780055W	M1780054U	9/28/04	M18/M13
	Si	M1780053V	1000	1.00		5.00		SD 9/24/04	R	M1780055W	M1780054U	9/25/04	M18/M17
	Sr	M1780050V	1000	0.500		2.50		SD 9/27/04	S	M1780055W	M1780054U	9/28/04	M18/M17
								SD 9/28/04	T	M1780055W	M1780054U	9/29/04	M18/M17
									U				
									V				
									W				

STANDARD OPERATING PROCEDURE

for

DETERMINATION OF MERCURY IN SOLID OR SEMISOLID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY FOR INDIANA PINES SITE

SOP No.: MET-7471APines

Revision: 0

September 23, 2004

Approved by: Christine Kutzer (Supervisor) — Date: 9/23/04

Lisa Reyes (QA Coordinator) — Date: 9/23/04

Michael K. Perry (Laboratory Director) — Date: 9/23/04

One Mustard St, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

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1. SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 7471A to determine the concentration of mercury in soils, sediments, bottom deposits and sludge-type materials. The range of the method is 0.2 to 10 ug/L. The range may be extended above or below the normal range by increasing or decreasing the sample size. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A known portion of a soil sample is transferred to a hot block cup. It is digested in diluted potassium permanganate solution and oxidized for thirty minutes at 95°C. Mercury in the digested water sample is reduced with stannous chloride to elemental mercury and measured by the conventional cold vapor atomic absorption technique.

3. DEFINITIONS

3.1. **Calibration Blank** - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to auto-zero the instrument.

3.2. **Calibration Standard** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicate sample indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4. **Laboratory Control Sample (LCS)** - An aliquot of an ERA soil sample with a known concentration. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.5. **Matrix Spike (MS)** - An aliquot of an environmental sample to which a known quantity of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

3.7. **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear.

3.8. **Method Detection Limit (MDL)** - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

3.9. **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.

3.10. **Batch** - Unit of samples prepared together on the same day, not to exceed 20 samples.

4. HEALTH AND SAFETY WARNINGS

The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents.

All contact with mercury should be avoided. Mercury vapor is especially toxic, causing severe respiratory tract damage. Chronic exposure to mercury through any route can produce central nervous system damage. May cause muscle tremors, personality and behavior changes, memory loss, metallic taste, loosening of the teeth, digestive disorders, skin rashes, brain damage and kidney damage. Can cause skin allergies and accumulate in the body. Repeated skin contact can cause the skin to turn gray in color. A suspected reproductive hazard; may damage the developing fetus and decrease fertility in males and females.

5. CAUTIONS

- Because of the extreme sensitivity of the analytical procedure and the presence of mercury in a laboratory environment, care must be taken to avoid extraneous contamination. Sampling devices, sample containers and plastic items should be determined to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contamination from airborne mercury vapor.

- Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks

6. INTERFERENCES

6.1. Interferences have been reported for soils containing sulfide, chloride, copper and tellurium. Organic compounds, which have broad band UV absorbance (around 253.7 nm), are confirmed interferences. The concentration levels for interferants are difficult to define.

6.2. Low level mercury sample preparation, digestion, and analysis may be subject to environmental contamination if preformed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent in analyses such as chemical oxygen demand (COD).

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in any subject and have successfully completed an Initial Demonstration of Capability after training using the Training Plan Form (found on the CAS Intranet). Training and Demonstration of Capability are in accordance with NELAC 2002 Standard.

8. EQUIPMENT AND SUPPLIES

8.1. Perkin Elmer FIMS - Atomic Absorption Spectrophotometer equipped with a vapor generator, quartz absorption cell and mercury hollow cathode lamp.

8.2. 50mL hot block cups and caps

8.3. 100 mL B-Cups and caps

8.4. Hot Block capable of maintaining a digestion temperature of 90-95°C.

8.5. Pipettes and graduated cylinders.

8.6. Mercury stock solution (1,000 mg/L) - Purchased. Store at room temperature. Dispose per manufacturer's expiration date.

8.7. Intermediate Stock Solution (10 mg/L) - Prepare a 1/100 dilution of the 1000mg/L Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Store at room temperature for up to 1 week.

8.8. Working Solution (100 µg/L) - Prepare a 1/100 dilution of the 10mg/L Intermediate Stock Solution in a volumetric flask and dilute with DI water. Acidify with 0.5 ml of concentrated HNO_3. Prepare fresh each day analysis is performed.

8.9. Calibration Standards - Prepare 0, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 ug/L calibration curve. Transfer 0, 0.1, 0.25, 0.5, 1.0, 2.5, 5.0 mL aliquots of the 100 µg/L working solution to a series of labeled hotblock cups. Add the appropriate amount of reagent water to bring each cup to a final volume of 5 ml. Add 5 ml of aqua regia. Loosely cap each cup. Prepare 2 blank standards to ensure sufficient volume for the analysis. The CRDL standard is prepared as the 0.2 standard.

8.10. ASTM Type II water

8.11. Concentrated Nitric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.12. Concentrated Sulfuric Acid – Metals Grade, purchased commercially. Expires as per manufacturer's indications.

8.13. Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

8.14. 5% w/v Potassium Permanganate Solution - Dissolve 50 g of $KMnO_4$ in 1 L of reagent water. Store at room temperature for up to 6 months.

8.15. 12% w/v Sodium chloride-hydroxylamine chloride solution - Dissolve 120 g of NaCl and 120 g of hydroxylamine hydrochloride (NH_2OH*HCl) in 1 L of reagent water. (Hydroxylamine sulfate $(NH_2OH)_2$ H_2SO_4 may be used in place of hydroxylamine hydrochloride.) Store at room temperature for up to 6 months.

8.16. 1.1% Stannous chloride + 3% HCl solution - Add 11.0 g of $SnCl_2$*$2H_2O$ to 1 L of 3% HCl. Prepare daily.

8.17. The calibration blanks (ICB and CCB), prepared daily, must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

8.18. The preparation blank (PB) is prepared in the same manner as the calibration blank and is carried through the entire preparation scheme with each batch of samples to be analyzed.

8.19. With each batch of samples to be analyzed, prepare a laboratory control sample (LCS) by weighing a 0.60g portion of an ERA soil standard and place in the bottom of a 50 mL hotblock cup. The LCS must be carried through the entire sample preparation scheme.

8.20. Initial / Continuing Calibration Verification Standard (ICV/CCV) 3.0 ug/L - Prepare an intermediate stock solution and working solution of 10 mg/L and 100 µg/L using a different stock source than the calibration standards. Transfer 1.5 ml of 100 µg/L solution (prepared daily) to a 50 ml hotblock cup. Add 3.5 ml of reagent water and 5 ml of aqua regia. Prepare 2 CCVs to ensure sufficient volume for the analysis.

8.21. The matrix spike sample (MS) is prepared by fortifying a 0.6g sample with 0.5 ml of 100 µg/L CCV standard in a hotblock cup. Carry through the entire digestion and instrument procedure as a routine sample.

9. PROCEDURE

9.1. Calibration and Standardization

Calibration Standards for the initial calibration must be prepared with each daily analysis. A blank and 5 standards is required. The correlation coefficient for each calibration must ≥0.995.

9.2. Sample Collection

Samples are to be collected in purchased, certified clean glass or plastic sample jars.

9.3. Sample Handling and Preservation

9.3.1. Maintain at 0-6°C from receipt until analysis.

9.3.2. Digested and analyze samples within 28 days of collection. Once digested, samples are analyzed as soon as possible.

9.3.3. Sample handling, storage, and custody procedures are in compliance with NELAC 2002 Standard.

9.4. Sample Preparation

9.4.1. Weigh 0.6g portion of a representative sample (approx. 0.2g portions from three areas of the sample) and place in the bottom of a hot block cup. Add 5 ml of reagent water and 5 ml of aqua regia. Loosely cap the sample cup.

9.4.2. Heat in the hotblock for 2 minutes at 95°C. Cool, then add 25 ml of reagent water and 15 ml of 5% potassium permanganate solution. Mix thoroughly and place in the hotblock for 30 minutes at 95°C.

9.4.3. Note: Samples with high organic content may required additional permanganate. Shake and add additional permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Ensure that equal amounts of permanganate are added to all samples, standards and blanks.

9.4.4. Cool and add 3.0 ml of 12% sodium chloride/hydroxylamine hydrochloride solution. Add 25 ml of reagent water and the samples are now ready to be analyzed. The stannous chloride solution is added automatically by the vapor generator.

9.5. Sample Analysis

9.5.1. Analyze the standards and samples using the Perkin Elmer Flow Injection Mercury System. See Operations Manual for details.

9.5.2. Sample concentrations exceeding the Linear Range require sample dilution. Dilutions should be performed so that the instrument concentration will fall in the mid-range of the calibration curve.

9.6. Troubleshooting

All maintenance activities are recorded in a maintenance logbook kept for each instrument. CAS staff performs most routine maintenance and troubleshooting. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Typical preventive maintenance measures include, but are not limited to, the following items:

- Check gases and tubing, daily
- Check optic tubes and filter membrane for moisture before analysis

9.7. Data Acquisition, Calculations, and Data Reduction Requirements

Calculations:

From the prepared calibration curve compute sample values by comparing response with the standard curve. Calculate the mercury concentration in the sample in mg/Kg by using the formula:

mg/Kg = Vol. (ml)/sample Wt(g) **x** 1mg/1000ug **x** 1L/1000ml **x** 1000g/1Kg **x** C **x** dilution

C = concentration of Hg in digestate, in ug/L

9.8. Computer Hardware and Software

- Personal Computer running Perkin Elmer AA Winlab for Window v.2.50
- Metals Analytical Review and Reporting System (MARRS) v.3.2.44
- StarLIMS v.6.11.a

10. DATA AND RECORDS MANAGEMENT

10.1. **Repsonsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the ICP analyst. The samples are analyzed for metals of interest using AA software. The results are transferred to MARRS (for reporting package work) and StarLIMS for validation, reporting, and invoicing.

10.3. **Data Review** – Data will be reviewed by the instrument analyst and a qualified peer using a data review checklist (attached).

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. Preparation Blanks must be analyzed at least once per batch of 20 or fewer samples. PB values must not exceed the MRL (method reporting limit). If the PB is out of control, fresh aliquots of the samples must be prepared and analyzed again for affected analytes after the source of the contamination has been corrected and acceptable PB values have been obtained.

11.2. Laboratory Control Samples assess laboratory performance against the required control limits. The control limit range is specific for each lot and is recorded on a certificate from the manufacturer. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Redigestion and analysis is required until acceptable LCS recovery is performed.

11.3. Calibration Verification Standards must immediately follow each calibration, after every tenth sample, and at the end of the sample run. Initial Calibration Verification must verify that the instrument is within ±10%. Continuing Calibration Verification standards must confirm the calibration within ±10% throughout the analyses. If the recovery of mercury falls outside the required control limits, the analysis is judged to be out of control, and the source of the problem should be identified and resolved before continuing analysis. Reanalysis of any sample(s) associated with the outlying ICV or CCV standards is required. All samples must be bracketed with acceptable ICV and CCV standards.

11.4. Sample Matrix Accuracy and Precision are assessed based upon MS and Duplicated performance. Refer to Appendix C of the Quality Assurance Manual for frequency and QC criteria per method of analysis. If the MS is out of control and the LCS is in control, assume matrix interference and flag the associated data.

11.5. Method Detection Limit (MDL) - A mercury MDL must be determined annually using 7 replicates of a fortified blank solution at a concentration of 2-3 times the estimated detection limit. Practical Quantitation Limits (PQLs) are calculated from the MDL by multiplying the MDL by a factor of at least 3. The PQLs are generally used as CAS Reporting Limits. To determine the MDL, refer to 40 CFR Part 136 Appendix B.

12. REFERENCES

- *Test Methods For Evaluating Solid Waste, Physical/Chemical Methods*. USEPA SW-846, 3rd Edition, September 1994.

- *Methods For the Determination of Metals in Environmental Samples Supplement I.* USEPA/600/R-94/111, May 1994

- EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW No. ILM04.0.

- Analytical Services Protocol (ASP), New York State Department of Environmental Conservation, December 1995.

- 40 CFR Part 136 Appendix B

- NELAC 2002 Standard.

Columbia Analytical Services

Analysis For: Hg | EPA Method: 7470 / 7471 / 245.1 / 245.5 | Analyst: ____________

[illegible]h Temp: In____/ Out____ | Report: Routine / ASP / Pkg.5 | Date Prepped: ____________

Time In: ________ | File Name: ________ | Date Analyzed: ____________

Time Out: ________

	Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)		Client / Submission #	Sample Number	Initial Wgt/Volume (g/ml)	Final Volume (ml)
1					31				
2					32				
3					33				
4					34				
5					35				
6					36				
7					37				
8					38				
9					39				
10					40				
11					41				
12					42				
13					43				
14					44				
15					45				
16					46				
[illegible]					47				
[illegible]					48				
19					49				
20							ICB	100ml DI Water	100
21							Std 0	100ml DI Water	100
22							Std 0.2*	0.20ml of 0.1ppm	100
23							Std 0.5*	0.50ml of 0.1ppm	100
24							Std 1.0*	1.00ml of 0.1ppm	100
25							Std 2.0*	2.00ml of 0.1ppm	100
26							Std 5.0*	5.00ml of 0.1ppm	100
27							Std 10.0*	10.0ml of 0.1ppm	100
28							ICV/CCV**	3.00ml of 0.1ppm	100
29							LCSW/MS**	1.00ml of 0.1ppm	100
30							CRDL*	0.20ml of 0.1ppm	100

Lot # of Reagents Used:

HNO3: ____________ H2SO4: ____________ HCL: ____________ K2S2O8: ____________ KMnO4: ____________

SnCl2: ____________ NaCl: ____________ NH2OH-HCL: ____________ LCSS CAS Lot#: __________

LCSS ERA Lot#: __________

*Source Standard: (Vendor/Lot #)____________
*(10ppm stock Lot#: ______________)
*(0.1ppm working std Lot#: __________)

**ICV Standard: (Vendor/Lot #)____________
**(10ppm stock Lot#: ______________)
**(0.1ppm working std Lot#: __________)

Comments/Problems: ____

Batch Name: ____________ ____________

Metals Instrument Analysis Training Plan

Procedure:____

SOP:______________ Revision:_________ Date:________

Trainee:____________________

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
-the chemical and physical principals behind the measurement by the instrument

Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs

-ADM-BATCHSEQ	-ADM-PCAL	-ADM-SIGFIG
-ADM-DATAENTRY	-ADM-DIL	-ADM-SPSR
-ADM-MDL	-ADM-DREV	-ADM-TRANDOC

Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
-standard and reagent prep and documentation – including pipet used
-instrument power up and warm-up
-instrument set-up, daily maintenance and checks
-use and loading of autosampler
-sample analysis including:
    -calibration
    -sample dilution
    -software command of instrument
    -use of QC samples and QC criteria
    -common troubleshooting
-instrument logbook use
-data reduction, reporting, and review

Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

Signature:________________________ Date:__________

6. Perform SOP with supervision
- including all items in 4.

Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
-all of the item listed in 4
-IDC (4 mid-range standards performed before client samples are analyzed)
-attach IDC certificate, raw data, and summary spreadsheet.

Trainer:____ Trainee:____ Date:____

Columbia Analytical Services inc.
An Employee-Owned Company

METALS DEPARTMENT
DATA QUALITY CHECKLIST

Data File:______________ Run Date:______________ Instrument:______________

Methods Used:
ICP- 200.7 // 6010B // ASP/CLP // NIOSH
GFAA- EPA 200 Series // SW846 // ASP/CLP
CVAA- EPA 200 Series // SW846 // ASP/CLP

Batch ID / Metals Reviewed:____

____

Yes	No	NA			Yes	No	NA
☐	☐	☐	1.	**Holding Times met method requirements?** ICP / GFAA- 6mths from sampling to analysis Hg- 28 days from sampling to analysis (26 days from VTSR)	☐	☐	☐
☐	☐	☐	2.	**ICAL met method requirements?** Correlation Coefficient > or = 0.995 ICP High Check= 95-105%	☐	☐	☐
☐	☐	☐	3.	**ICV acceptable?** ICP: 200.7= 95-105% ; NIOSH / 6010B / ASP/CLP= 90-110% GFAA: EPA 200 Series / SW846 / ASP/CLP= 90-110% Hg: EPA 200 Series= 95-105% ; SW846 / ASP/CLP= 90-110%	☐	☐	☐
☐	☐	☐	4.	**CCVs acceptable? Analyzed per 10 samples?** ICP: 200.7 / 6010B / ASP/CLP / NIOSH= 90-110% GFAA: EPA 200 Series= 90-110% ; SW846 / ASP/CLP= 80-120% Hg: EPA 200 Series= 90-110% ; SW846 / ASP/CLP= 80-120%	☐	☐	☐
☐	☐	☐	5.	**CCBs accepttable? Analyzed per 10 samples?** Concentrations < RL	☐	☐	☐
☐	☐	☐	6.	**Method Blank results <RL?**	☐	☐	☐
☐	☐	☐	7.	**LCS recoveries within QC limits?** ICP: 200.7= 85-115% ; 6010B / ASP/CLP / NIOSH= 80-120% GFAA: EPA 200 Series= 85-115% ; SW846 / ASP/CLP= 80-120% Hg: EPA 200 Series= 85-115% ; SW846 / ASP/CLP= 80-120% LCSS (soil) Certificate of Analysis QC limits per manufacturer	☐	☐	☐
☐	☐	☐	8.	**All sample concentrations within LR?**	☐	☐	☐
☐	☐	☐	9.	**MS recoveries within QC limits?** ICP: 200.7= 70-130% ; 6010B / ASP/CLP= 75-125% GFAA: EPA 200 Series / SW846 / ASP/CLP= 75-125% Hg: EPA 200 Series= 70-130% ; SW846 / ASP/CLP= 75-125%	☐	☐	☐
☐	☐	☐	10.	**Duplicate RPD within QC limits?** 20% for RPD shall be used for samples > or = 5 times the RL. RL shall be used for samples < 5 times the RL.	☐	☐	☐
☐	☐	☐	11.	**Is GFAA Post Digest Spike within 85-115%?**	☐	☐	☐
☐	☐	☐	12.	**Dilution factors verified and calculated correctly?**	☐	☐	☐
☐	☐	☐	13.	**Bench Sheet complete, initials, date, and time:**	☐	☐	☐
☐	☐	☐		•Are standards and reagents traceable?	☐	☐	☐
☐	☐	☐		•Is unused space on the sheet crossed out?	☐	☐	☐

Analyst:________________ Peer Review:________________
Date:________________ Date:________________

COMMENTS:
****Comments must be provided for any items noted above as "No"**

STANDARD OPERATING PROCEDURE

for

METALS DIGESTION, WATERS FOR GFAA ANALYSIS

SOP No.: MET-3020Amod

Revision: 3

April 4, 2002

Approved by: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: ___________
Initials: ______ Date: ___________
Initials: ______ Date: ___________

DOCUMENT CONTROL

NUMBER: _________________

Initials: ______ Date: ___________

1 SCOPE AND APPLICATION

Method 3020 is an acid digestion procedure used to prepare surface and ground water samples for analysis by graphite furnace atomic absorption for dissolved and total recoverable metals analysis.

2 METHOD SUMMARY

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Nitric Acid is used as the final reflux acid for most Graphite Furnace analyses.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Water (LCSW)** - An aliquot of reagent water to which known quantities of the method analytes are added. The LCSW is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 INTERFERENCES

See appropriate analytical SOP for applicable interferences

5 SAFETY

5.1 Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment, including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

6 SAMPLE COLLECTION, PRESERVATION AND STORAGE

For aqueous samples, glass or plastic sample containers are acceptable. Sample volume should be acid preserved with (1+1) nitric acid to pH<2. Samples must be analyzed within 6 months of sample collection. Additional sample handling policies and procedures are discussed in SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 250 ml or 100 ml beakers
7.2 Ribbed watch glasses
7.3 Hot plates
7.4 Graduated cylinders
7.5 Eppendorf Pipettors
7.6 Class A Volumetric Pipets
7.7 Hot Block digestor with ETR-3200 Controller by Environmental Express, LTD.
7.8 Graduated block digestor sample cups with screw caps or snap down caps.
7.9 Block digestor ribbed watch glasses or reflux cap
7.10 CPI MOD Block Digestor.

8 PREVENTIVE MAINTENANCE

All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Reagent Water - ASTM Type II water

9.2 Concentrated nitric acid (Baker Instra-Analyzed 69-70%). Acid should be analyzed prior to use to demonstrate the acid is free of impurities. Store at room temperature in the dark. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.3 Hydrogen Peroxide (30%) - H_2O_2 should be demonstrated to be free of impurities. Purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.4 Metals spiking solutions - See Table 1- purchased commercially. Expires as per manufacturer's indications or 3 years from receipt, whichever occurs sooner.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURES

11.1 HOT PLATE

11.1.1 For non CLP furnace waters, shake the samples and measure a 50 mL aliquot into a 250 mL or 100mL beaker. Rinse the cylinder three times to ensure quantitative transfer of the sample. At this point use a calibrated eppendorf pipet to add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

11.1.2 Add 3mL of conc. HNO_3 and 1mL of 30% H_2O_2. Cover with a watch glass.

11.1.3 Heat on a hot plate at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony easily lost by volatilization.

11.1.4 Remove the beaker from the hot plate and allow to cool. Rinse down the sides of the beaker and the watch glass with DI water and transfer the digestate to a graduated cylinder. Dilute to final volume of 50 mL.

11.1.5 Allow digestates to settle before analysis.

11.2 HOT BLOCK DIGESTOR

11.2.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

11.2.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

11.2.3 Label graduated hot block digestor sample cups with appropriate sample ID's for digestion. Shake the sample and measure 50 mL aliquot into the designated graduated hot block digestor sample cup. At this point use a calibrated eppendorf pipet to add the appropriate spiking solutions (Table 1) directly into the designated spike sample prior to addition of reagents.

11.2.4 Add 3ml of conc. HNO_3 and 1.0 mL of 30% H2O2. Cover the sample with a disposable ribbed watch glass and place in Block Digestor at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization.

11.2.5 Cool the sample and dilute sample to 50ml in the graduated hot block digestor sample cup. Cover with screw cap and mix well. Place label on screw cap.

12 QA/QC REQUIREMENTS

12.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate dilution of metals spike solution (see Table 1).

12.2 Each day, prepare one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use 50 mLs D.I. water and follow the digestion procedures.

12.3 Each day, prepare one duplicate and spike sample per each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements. Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

12.4 Monitor sample temperature once during digestion (approximately 1.5 hours into the digestion) and record on the digestion log.

12.5 See appropriate analytical SOP and Appendix C of the Quality Assurance Manual for applicable QC limits and corrective action.

13 DATA REDUCTION AND REPORTING

13.1 Digestion logs are used to record all sample volumes, spike volumes, sample batch temperature etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached).

13.2 Data Review policies and procedures are discussed in ADM-DREV.

14 METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15 WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1 Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

15.2 Acidic waste is poured down the drain with copious amounts of water.

15.3 Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste, see SMO-SPLDIS.

16 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18 REFERENCES

18.1 “Test Methods For Evaluating Solid Waste, Physical/Chemical Methods”. EPA SW846, Third Edition, July 1992.

19 TRAINING OUTLINE

19.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2 Observe Sample Preparation. Follow Training Plan Form.

19.3 Participate in the methodology, documentation, and data reduction with guidance.

19.4 Perform an Initial Demonstration of Capability (IDC) by performing the analysis independently and analyzing a known standard four times. Recovery must be within acceptable limits. Complete summary spreadsheet, IDC certification form, and Training Plan Form. File forms with QA.

19.5 Continuing capability shall be demonstrated annually using an outside PE source, an internal unknown, or a new 4 replicate study.

20 METHOD MODIFICATIONS

Hydrogen peroxide has been added to the preparation procedure to provide a more complete digestion.

21 INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

22 ATTACHMENTS

- Table 1 Spike Concentrations
- Digestion Log Benchsheet
- SW846 Method 3020 Flow Chart

23 CHANGES FROM PREVIOUS REVISION

- Changed LCSS to LCSW (3.2) since this is a prep method for waters.
- Added storage and expiration to reagents (9) where needed.
- Changed the volume which the samples are to be reduced to before removing from the hot plate from 15-25 to 15-20 mL.
- Changed 11.2.1 to be less specific about what temperature to set the digestor and more focused on the temperature of the samples.
- Added reference to Appendix C of the QAM in QA/QC (12)
- Added need to monitor sample temperature during digestion and record on the prep sheet (13.1 and 12.4)
- Added Sections 14, 16, 17 and 20 for NELAP compliance.
- Added references to ADM-TRANDOC and the Training Plan Form to the Training Section (19)
- Changed attachment of digestion log benchsheet to include ILM 4.1.

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE #4 Furnace Spike			0.500ml Spk #4	to Final Volume of 50ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AS	4		**SB**	5
PB	2		**TL**	5
SE	1		**-**	-

SW846 Method 3020
Flow Chart

Non-CLP Furance Waters

**Mix Sample.
Transfer 50mL of sample to beaker and add 3mL conc. HNO_3 1mL (30%) H_2O_2.
Cover with watch glass.**

↓

Reflux gently and evaporate to approximately 15-20mL.

↓

Cool the beaker

↓

Dilute to 50mL with DI water, rinsing the sides of the beaker.

CAS-Rochester GFAA Water Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: ____________ **Date:** ________ **Spk Witness:** ________

Prep Method: **3020 modified // CLP** **Report Type:** **Routine // ASP // Pkg5**

Digest: **Initial // Redigest of:** ____________ **Approval:** ________

	Submission / Order #	pH	Initial Vol (ml)	Final Vol (ml)	Initial Color / Clarity	Final Color / Clarity	Metals	Spike Vol (ml)
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								

Spiking Standards / Reagent Lot #:
Spike 4: ________
HNO3: ________ H2O2: ________

Color / Clarity Key:
Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown
BL = Black ; **G** = Grey
Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque

Comments: ____________

STANDARD OPERATING PROCEDURE

for

METALS DIGESTION, SOILS, SEDIMENTS, AND SLUDGE FOR ICP AND GFAA ANALYSIS

SOP No.: MET-3050B

Revision: 3

January 15, 2003

Approved by: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: __________

1 SCOPE AND APPLICATION

Method 3050 is an acid digestion procedure used to prepare matrices such as soils, sludges, or sediments for analysis by ICP or graphite furnace atomic absorption.

2 METHOD SUMMARY

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid for ICP analyses. Nitric Acid is used as the final reflux acid for most Graphite Furnace analyses.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates and indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS) -** An aliquot of a soil to which known quantities of the method analytes are added by an outside vendor. The LCSS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 INTERFERENCES

4.1 See appropriate analysis SOP for applicable interferences

5 SAFETY

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

6 SAMPLE COLLECTION, PRESERVATION AND STORAGE

For non-aqueous samples, glass or plastic sample containers are acceptable. Samples are analyzed within 6 months of sample collection. Additional sample handling policies and procedures are in SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 250 and 100 mL beakers
7.2 Ribbed watch glasses
7.3 Hot plates
7.4 Graduated cylinders
7.5 Eppendorf Pipettors
7.6 Funnels
7.7 Mortar and pestle
7.8 Tongue depressors
7.9 Filter paper
7.10 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
7.11 Graduated block digestor ribbed watch glasses
7.12 Block Digestor Filters.
7.13 CPI MOD Block Digestor

8 PREVENTIVE MAINTENANCE

8.1 All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Reagent water - ASTM Type II deionized water. Reagent water must be interference free.

9.2 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the dark. Expires per manufacturer’s indications or one year from receipt, whichever is sooner.

9.3 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Acid should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature. Expires per manufacturer’s indications or one year from receipt, whichever is sooner.

9.4 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt, whichever is sooner.

9.5 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt, whichever is sooner.

9.6 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expires upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURES

11.1 HOT PLATE

11.1.1 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

11.1.2 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into a 250 or 100 mL beaker. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

11.1.3 Unless specified by project or state requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3, cover with a ribbed watch glass and reflux for 15 minutes. The sample temperature should be 90-95^{o}C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

11.1.4 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the beaker.

11.1.5 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

11.1.6 If the sample is being prepared for analysis by ICP, add 10 mL 1:1 HCL. If the sample is being prepared for analysis by Graphite Furnace no HCl is added.

11.1.7 Cover and reflux the ICP samples for 15 minutes without boiling. Allow to cool.

11.1.8 Prepare filters by rinsing with 1:1 nitric acid and DI.

11.1.9 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and watch glass with DI into the filter. Rinse the filter with DI. Bring to volume with DI.

11.2 HOT BLOCK DIGESTOR

11.2.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

11.2.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

11.2.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

11.2.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

11.2.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

11.2.6 Unless specified by project or state requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and for ICP only add 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

11.2.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

11.2.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

11.2.9 If the sample is being prepared for analysis by ICP, add 10 mL 1:1 HCL. If the sample is being prepared for analysis by Graphite Furnace no HCl is added.

11.2.10 Cover and reflux the ICP samples for 15 minutes without boiling. Allow to cool.

11.2.11 Prepare filters by rinsing with 1:1 nitric acid and DI.

11.2.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

12 QA/QC REQUIREMENTS

12.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

12.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

12.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

12.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

12.5 See appropriate analysis SOP for applicable QC limits and corrective action.

13 DATA REDUCTION AND REPORTING

13.1 Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

13.2 Reporting and method performance is discussed in the appropriate analysis SOP. Data review is discussed in ADM-DREV.

14 METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15 WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1 Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

15.2 Acidic waste is poured down the drain with copious amounts of water.

15.3 Samples with analyte concentrations exceeding TCLP regulatory limits are disposed of as hazardous waste. Others are dumped down the drain with plenty of water. See SMO-SPLDIS.

16 CORRECTIVE ACTION FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

19 TRAINING OUTLINE

19.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2 Observe Sample Preparation.

19.3 Participate in the methodology, documentation, and data reduction with guidance.

19.4 Complete a Training Plan Form for the procedure.

19.5 Show Initial Demonstration of Capability (IDC) by independently preparing and digesting four LCSs, or equivalent, according to the test method either concurrently or over a period of days. If recovery is within acceptable limits, complete IDC certification form, and Training Plan forms and file with QA. Continued capability shall be demonstrated annually using PE results, a single blind, or a new 4 replicate study.

20 METHOD MODIFICATIONS

None

21 INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

22 ATTACHMENTS

Table 1 Spike Concentrations
Digestion Log Benchsheets
SW846 Method 3050 Flow Chart

23 CHANGES FROM PREVIOUS REVISION

- Added Hot Block digestion procedures (11) and associated items to Apparatus and Equipment (7)
- Added sections 14, 16, 17, and 20 for NELAP compliance
- Changed the amount of time to reflux sample from 10-15 minutes to just 15 minutes after the first addition of acid (11).

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A			1.00ml Spk A	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AL	200		**NI**	50
AS	4		**SE**	1
BA	200		**AG**	5
BE	5		**TL**	200
CD	5		**V**	50
CR	20		**ZN**	50
CO	50		**B**	100
CU	25		**CA**	200
FE	100		**MG**	200
PB	50		**NA**	2000
MN	50		**K**	2000

SPIKE SOLUTION B			1.00ml Spk B	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SB	50		**TI**	50
MO	50		**-**	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml		**INDIVIDUAL METALS**	0.5ml Spk. to Final Volume of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
SE	1000		**SN**	1000

SPIKE #4 Furnace Spike			1.00ml Spk #4	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***		***Metal***	***Conc. (ug/mL)***
AS	4		**SB**	10
PB	2		**TL**	5
SE	1		**CU**	0.5

CAS-Rochester ICP Soil Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: ____________ **Date:** ______

Spike Witness / Lot Approval: ____________

Prep Method: SW846 3050 // CLP

Batch Temp:

Digest: Initial // Redigest of: ____________

Report Type: Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: ________ Spike #4: ________
TCLP Spk: ________ TCLP Ba: ________
Se Std: ________ Sn Std: ________
HNO3: ________ HCL: ________
H2O2: ________ LCSS: ________

Color / Clarity Key:
Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown
BL = Black ; **G** = Grey ; **W** = White
Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque
Texture: **F** = Fine ; **M** = Medium ; **CS** = Coarse ; **NAQ** = Non Aqueous

01

Comments: ____________________

CAS-Rochester Furnace Soil Digest Log

Analyst:__________ **Date:**____________ **Spike Witness:**________ **Approval:**________

Method: SW846 3050 // CLP   Digest: Initial Digestion // Redigestion of _______________

Report: Routine // ASP // Pkg.5   **6010B/846 // 200.7/136 // ASP/CLP**

	Client/ Order #	Initial wgt(g)	Final vol(ml)	Initial Color/Clarity	Final Color/Clarity	Metals	Spike vol(ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							

Spiking Standards Lot # or Prep Date:
Spike #4__________

Reagent Lot #:
LCSS__________ HNO3__________ H2O2__________

0091

Comments/Problems:____

____

SW846 Method 3050
Flow Chart

Non-CLP Soils, Sediments and Sludges

Mix sample. Weigh 1.0-1.5g of sample. Add 10mL (1:1) HNO3 and for ICP only add 1.5 mL 1:1 HCl, mix to a slurry and cover with a watch glass.

↓

Gently reflux 15min.

↓ *Cool*

Add 5mL conc. HNO3 and reflux for 30 min. Repeat.

↓

Evaporate to 5mL.

↓

Add 2mL DI and 3mL 30% H2O2. Warm gently to start effervescence.

↓

If efferv. doesn't subside, add 3mL portion of 30% H2O2 (followed by warming). Add 1 mL portions until efferv subsides. Don't add more than a total of 10mL 30% H2O2.

↓

Type of Digest

Furnace: Evaporate to approximately 5mL

ICP: Add 5mL conc. HCL and 10mL DI Reflux 15min.

↓

Filter into grad cylinder, Collecting DI rinses of beaker and watch glass

↓

Dilute to 100mL with

DI water.

STANDARD OPERATING PROCEDURE

DETERMINATION OF TRACE METALS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAA)

SOP Code: MET-GFAA

Revision: 3.0

September 27, 2001

Approved by: ______________ 11/1/01
Department Manager — Date

______________ 11/1/01
Quality Assurance Coordinator — Date

______________ 11/1/01
Laboratory Director — Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: DCB Date: 12/20/02
Initials: DCB Date: 12/19/03
Initials: DCB Date: 12/14/04

DOCUMENT CONTROL
NUMBER: MET-002
Initials: [illegible] Date: 11/2/01

1.0 SCOPE AND APPLICATION

1.1 This procedure describes the procedure for the analysis of soil, sludge and water digestates by graphite furnace atomic absorption (GFAA) spectrometry. Typically, this procedure is applicable to the analytes and EPA methods listed in Table 1. Other elements may be determined when reference is made to the applicable published method. All analytical methods used are in accordance with EPA methods from SW-846 and EPA 200 Series, the EPA Contract Laboratory Program (CLP) statement of work (SOW), and the NYSDEC Analytical Services Program (ASP).

1.2 The Practical Quantitation Limits (PQL) are listed in Table 1. The reported PQL may be adjusted if required for specific project requirements, however, the capability of achieving other reported PQLs must be demonstrated. Results may be reported to the Instrument Detection Limits (IDLs) upon request. IDLs are updated quarterly. The Method Detection Limits (MDLs) are updated annually and are available upon request.

2.0 METHOD SUMMARY

2.1 Prior to analysis, samples must be digested using appropriate sample preparation methods. A representative aliquot of sample is prepared as described in the applicable digestion SOP. Refer to the following Metals Digestion SOPs:

MET-3005A	Metals Digestion, Waters, Total Recoverable and Dissolved for ICP
MET-3010A	Metals Digestion, Waters for ICP
MET-3020A	Metals Digestion, Waters for GFAA
MET-3050B	Metals Digestion, Soils, Sediments and Sludges for ICP and GFAA
MET-CLP	Metals Digestion, Waters and Soils for CLP

2.2 The digestate is analyzed for the element(s) of interest, using GFAA conditions (See Instrument Specifications by Metal Manual in the GFAA lab) for the element to be determined. Absorbance is measured as a function of element concentration.

2.3 For GFAA analyses by CLP procedures, see the applicable CLP SOW or ASP.

3.0 DEFINITIONS

3.1 **Analytical Sequence** - Samples are analyzed in a set referred to as an analytical sequence. The sequence begins with instrument calibration followed by analysis of sample digestates interspersed with analysis of calibration verification standards.

3.2 **Initial Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.3 **Matrix Spike** (MS) - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected.

3.4 **Duplicate Sample** (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.5 **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.6 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7 **Instrument Blank (CCB)** - The instrument blank (also called continuing calibration blank) is a volume of blank reagent of composition identical to the digestates. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

4.0 INTERFERENCES

Interferences are dealt with through the use of matrix modifiers (commonly Ni and Pd) and post digestion spikes. Detailed discussion of interferences may be found in the applicable EPA method.

Interferences from contaminated reagents must be eliminated. The purity of acids must be established by the laboratory as being high enough to eliminate the introduction of contamination above the Method Detection Limit.

5.0 SAFETY

Normal precautions as per the CAS EH&S Manual are to be followed. In addition, because acids are used in the procedure, there is a danger of exposure to corrosives. Sufficient care must be taken in handling acidic solutions. Safety glasses must be worn while preparing and handling the solutions. Gloves and a laboratory coat should be worn while handling samples, acids, and sample digestates.

6.0 SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

6.1 Either glass or plastic sample containers may be used.

6.2 All aqueous samples are preserved with nitric acid to a pH of <2.

6.3 Soil and aqueous samples for GFAA analyses by CLP procedures are stored at 0-6 °C. from time of receipt until digestion. Soil and aqueous samples for GFAA analyses by other procedures are stored at ambient temperature from time of receipt until digestion.

6.4 Holding time for samples for GFAA analyses is 6 months (sample collection to digestion).

6.5 Samples are received in the GFAA analysis laboratory as 0.5% nitric acid digestates. Sample digestates are stored in labeled plastic B-cups or Hot Block digestion vessels.

7.0 APPARATUS AND EQUIPMENT

7.1 Graphite furnace atomic absorption spectrophotometer (AAS). See Appendix A for element-specific instrument parameters.

7.2 Hollow Cathode Lamp (HCL) or Electrodeless Discharge Lamp (EDL) for each metal analyzed by this procedure.

7.2.1 Electrodeless Discharge Lamp power supply.

7.3 100-1000uL Eppendorfs

7.4 2 ml Beaker cups compatible with the AAS autosampler.

7.5 Volumetric flasks of suitable precision and accuracy.

8.0 PREVENTIVE MAINTENANCE

All maintenance activities are recorded in a maintenance logbook kept for each instrument. Most routine maintenance and troubleshooting is performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Typical preventive maintenance measures include, but are not limited to, the following items:

- Cleaning the quartz windows
- Changing the graphite tubes

- Cleaning the capillary tube
- Change filter in Separator Trap annually or if necessary
- Inspection and cleaning of electrodes, shroud, and cells as needed.

9.0 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Concentrated Nitric Acid – Metals Grade or higher to eliminate the introduction of contamination above the method detection limit.

9.2 Matrix Modifiers

Palladium Modifier Dilute 10 mls Palladium Nitrate (1%) plus 1.0 ml Magnesuim Nitrate (2%) with 100.0 ml DI. Expires within 6 months at room temperature. Used for arsenic, selenium, and thallium.

Ammonium Dihydrogen Phosphate (purchased) Dilute 1.0 g to 100 mls DI. Expires 6 months at room temperature. Used for lead analysis.

9.3 Standards

9.3.1 1000 ppm Stock Standards (AA Grade) - Commercially available certified solutions.

9.3.2 The GFAA Calibration Stock Standard is made by pipetting the volume of the 1000 ppm As, Pb, Se, and Tl stock standards shown in the table below, plus 0.50 ml of concentrated nitric acid into a 100 ml volumetric flask and diluting to volume with DI water. Prepare Calibration Stock Standard weekly.

Analyte	ml of Stock Std. (1000 ppm)	Add 0.50 ml conc. HNO_3 and dilute to	Final Concentration (mg/L)
Arsenic	0.50	100 ml	5.0
Lead	0.45	100 ml	4.5
Selenium	0.50	100 ml	5.0
Thallium	0.50	100 ml	5.0
Lead - DW	0.30	100 ml	3.0

9.3.3 The GFAA Calibration Working Standard is prepared by diluting 1.0 ml of the GFAA Calibration Stock Standard and 0.5 ml of concentrated nitric acid to 100 ml with DI water. Final concentrations range from 0.030 to 0.050 mg/L. Prepare calibration working standard fresh each day. LMR 8/23/02

insert table > see attached

9.3.4 The GFAA Initial and Continuing Calibration Verification (ICV andCCV) Stock Standard is made by pipetting the volume of the 1000 ppm As, Pb, Se, and Tl

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9.3.3 Continued…
"Prepare the calibration working standard fresh each day." This standard is loaded into the autosampler (typically location 38) so that the instrument may auto-dilute the working standard to prepare the calibration standards at four concentration levels intended for the initial curve (blank and 4 standards). The instrument makes the following dilutions according to the analyte being analyzed:

Element	Working Standard (ug/L)	Volume of Working Std. (uL)	Final Volume (uL)	Final Concentration (ug/L)
Arsenic	50	4	20	10
	50	8	20	20
	50	12	20	30
	50	20	20	50
Lead	30	3	30	3
	30	9	30	9
	30	15	30	15
	30	30	30	30
Antimony	50	6	30	10
	50	12	30	20
	50	18	30	30
	50	30	30	50
Selenium	50	3	30	5
	50	9	30	15
	50	18	30	30
	50	30	30	50
Thallium	50	4	20	10
	50	8	20	20
	50	12	20	30
	50	20	20	50
Copper	10	4	20	2
	10	8	20	4
	10	12	20	6
	10	20	20	10

stock standards shown in the table below, plus 0.50 ml of concentrated nitric acid into a 100 ml volumetric flask and diluting to volume with DI water. Prepare the ICV / CCV Stock Standard from a second source, weekly.

Analyte	ml of Stock Std. (1000 ppm)	Add 0.50 ml conc. HNO_3 and dilute to	Final Concentration (mg/L)
Arsenic	0.25	100 ml	2.5
Lead	0.20	100 ml	2.0
Selenium	0.25	100 ml	2.5
Thallium	0.25	100 ml	2.5
Lead - DW	0.14	100 ml	1.4

9.3.5 The GFAA CCV Working Standard is prepared by diluting 1.0 ml of the GFAA CCV Stock Standard and 0.5 ml of concentrated nitric acid to 100 ml with DI water. Final concentrations range from 0.014 to 0.025 mg/L. Prepare CCV working standard fresh each day.

9.3.6 The Continuing Calibration Blank (CCB) is prepared by diluting 5.0 ml of concentrated HNO_3 to 1000 ml with DI water.

10.0 RESPONSIBILITIES

It is the responsibility of the analyst to perform the analysis according to the instructions in this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are only to be performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

11.0 PROCEDURE

11.1 Instrument Operation and Data Acquisition Procedure

11.1.1 Instrument performance specifications are specified in the operations manual located in the GFAA Lab. Refer to these when setting the parameters for acquisition and select the set of parameters applicable to the element being measured. For Arsenic, Lead, Selenium, and Thallium, the gas type is 95% argon-5% hydrogen. The modifiers used are 500 ppm Pd and 500 ppm $Mg(NO_3)_2$.

11.1.4 Turn on computer and instrument. Install appropriate HCL or EDL lamp and turn on by going to the Align Lamps screen. Allow the Hollow Cathode Lamp to warm up atleast 15 minutes and the Electrodeless Discharge Lamp atleast one hour. This warm up time is used to insure maximium optimization is achieved.

11.1.5 Wipe down the autosampler tip before each analysis. Inspect and clean, if necessary, the electrodes, shroud, lens and cells. If the instrument has a fume extractor be sure the Separator Trap is filled with deionized water.

11.1.6 Select Automatic Run and choose the appropriate program for analysis.

11.1.7 Go to Align Lamp screen and optimize lamp alignment.

11.1.8 Insert sample analysis sequence into Instrument Run Log. Create Sample Information File (sample labels) from logbook. Open the Method Editor and go to the Checks page. Assign a post digestion spike to the proper samples by setting parameters where is asks "Perform Recovery Measurements".

11.1.9 Load autosampler wheel with standards, blank, modifier, and sample digestates being analyzed, being sure to identify samples by their autosampler position in the instrument log book.

11.1.10 Start automatic run.

11.1.11 Monitor the analytical run for calibration and sample abnormalities.

11.1.12 Dilutions for samples with results over the calibration range are to be made manually and added to the autosampler.

11.2 Calibration

11.2.1 The analysis begins with the analysis of calibration standards. Analyze an instrument blank and four calibration standards. The correlation coefficient for each calibration shall be checked to determine that the coefficient is equal to or greater than 0.995.

11.2.2 Following calibration, analyze an ICV standard. The resulting value must be within 95-105% of the true value for 200 Series metals and 90-110% of the true value for SW-846 and ASP / CLP4.1. If not, prepare new standards and recalibrate the system.

11.3 Sample Analysis

11.3.1 Following calibration, analyze samples and QC samples in an analytical sequence. Refer to the *SOP for Analytical Batches and Analytical Sequences.*

11.3.2 Prepare and analyze post-digestion spiked samples. For ASP / CLP4.1 analyses, all samples must be post-spiked and analyzed. For routine analyses, one sample per submission / job number is spiked and evaluated. If the spike recovery is outside the control limits of 85-115%, all the samples in the batch are post-spiked and analyzed. If spike recoveries are within the acceptable limits, analysis is continued with no further spiking. If the post-digestion spike is <40% recovery the sample is diluted by a factor of 5-10 and reanalyzed. If the post-digestion spike is between 40-85% and the sample concentration is less than half of the spike the data is reported. For CLP4.1 a "W" flag will be on the Form I when this occurs.

11.3.3 Method of Standard Additions (MSA) analysis is required when an outlying post-digestion spike recovery is between 40-85% or >115% AND the sample absorbance or concentration is less than 50% of the spike. Quantitation is bias to some unknown interference that has been confirmed and dilution and reanalysis does not improve performance, therefore MSA must be performed by analyzing the sample plus 3 spikes at 50, 100, and 150% of the sample concentration (single injection is only required). Plot a linear regression curve of concentration vs. absorbance and quantitate sample concentration from the curve. Refer to the CLP SOW or NYSDEC ASP for proper qualifications of sample data.

12.0 QA/QC REQUIREMENTS

12.1 All GFAA sample analyses shall be performed with duplicate burns and the average reported. Duplicate burns should not exceed 20%RSD to maintain precision throughout the run. If RSD exceeds 20%, reanalyze once; if continues to be >20%, dilute 1:2 and reanalyze to avoid interference.

12.2 The correlation coefficient for each calibration must be equal to or greater than 0.995. The software produces the calibration curve point by point and does not reject a calibration that has a correlation coefficient < 0.995. The run must be stopped by the operator if the correlation coefficient fails.

12.3 Analyze CCV standards and CCBs no less frequently then every ten samples in the analytical sequence.

12.3.1 For CCVs, the resulting value must be 90-110% of the true value for CLP analyses and 80-120% for routine analyses. If not, recalibrate the system and reanalyze samples run since the last acceptable CCV.

12.3.2 For CCBs, the resulting value must be less than the PQL. Check the CCB result for carryover. Re-analyze if the CCB result is above the PQL.

12.4 Each sample preparation batch must have a method blank associated with it. The method blank result should be < PQL. If not, redigest the batch of samples.

12.5 A laboratory control sample (LCS) is digested one per batch, or per 20 samples. The LCS recovery criteria is listed in Appendix C of the Quality Assurance Manual. If the LCS fails the acceptance criteria, redigest the batch of samples.

12.6 Post-digestion spike recovery acceptance limits are 85-115%. If outside these limits for the Preparation Blank stop analysis, correct problem and reanalyze. If routine sample recovery fails all samples in the corresponding submission / job # must be spiked. If post-spike recovery is > 40%, samples may be run by the method of standard additions to prevent further dilution see sections 11.3.2 and 11.3.3.

12.7 A duplicate sample is digested one per batch, or per 20 samples (one per 10 if 200 Series is requested). Frequency and QC criteria are listed in Appendix C of the Quality Assurance Manual. If the RPD is greater than the limit, determine if the sample is non-homogenous. Redigest if necessary, otherwise data may be flagged with a "*" for job specific QC samples.

12.8 A matrix spiked sample is digested one per batch, or per 20 samples. Frequency and QC criteria are listed in Appendix C of the Quality Assurance Manual. If outside acceptance limits, redigest if necessary, otherwise the data may be flagged with a "N" for job specific QC samples. If the sample concentration is >4x the spike level, no action is required.

12.9 Additional QC measures include annual determination of method detection limits. Refer to ADM-MDL for procedure and requirements.

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13.0 DATA REDUCTION AND REPORTING Refer to ADM-DREV for data review procedures.

13.1 Results for aqueous samples are calculated as follows and are reported in mg/L:

$$mg/L\ (sample) = C^* \times (Digestion\ Dilution\ Factor) \times (Post\text{-}Digestion\ Dilution\ Factor) \div 1000$$

13.2 Results for soil and solid samples are calculated as follows and are reported in mg/Kg.

$$mg/Kg\ (Sample) = C^* \times Post\ Digestion\ Dilution\ Factor \times \frac{Digestion\ Vol.\ (ml)}{Sample\ wt.\ (g)} \times \frac{1mg}{1000g} \times \frac{1L}{1000ml} \times \frac{1000g}{1Kg}$$

where C * is the concentration of the analyte as measured at the instrument in µg/L.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14.2 Excess, unused sample and testing byproducts are disposed following the procedures in the *SOP for Waste Disposal.*

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846, 3rd Edition; (September 1986) and Updates I (July 1992), II (September 1994), IIA (August 1993), IIB (January 1995), III (December 1996).

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, (Revised March 1993).

Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010 (June 1991) and Supplement I, EPA/600/R-94/111 (May 1994).

EPA Contract Laboratory Program, Statement of Work for Inorganic Analysis, SOW No. ILM04.0.

Analytical Services Protocol (ASP), New York State Department of Environmental Conservation, December 1995.

16.0 TRAINING OUTLINE

16.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry.

16.2 Observe Sample Preparation and Analysis.

16.3 Participate in the methodology, documentation, and data reduction with guidance.

16.4 Instrument Operation and Maintenance, if applicable.

16.5 Demonstrate Competency by performing the analysis independently. Analyze a known proficiency or standard four times to establish Initial Demonstration of Capability. If recovery is within acceptable limits, complete training form and certificate and file with QA. Continuing Demonstration of Capability is required on an annual basis, refer to ADM-TRANDOC.

17.0 INSTRUMENT-SPECIFIC ADDENDUM

See Operations Manual in GFAA Lab.

18.0 ATTACHMENTS

Table 1 Summary of Parameters, Methodology, and Reporting Limits

19.0 CHANGES FROM PREVIOUS REVISION

- Added reference to the Instrument Specifications per Metal Manual to Section 2.2.
- Changed Independent to Initial in Section 3.2
- Added reference to Hot Block digestion vessels in Section 6.5
- Added EDL Lamp and EDL power supply to Section 7
- Inserted how often the Calibration and ICV / CCV Standard Stocks should be prepared in Section 9.3.2 and 9.3.4
- Sections 11.0, 12.0 of previous SOP were revised to include more detail and referenced Appendix C of Quality Assurance Manual for QC criteria and frequency requirements.
- Deleted all references to analyzing Antimony by GFAA.

Table 1

Parameters, Methodology, and Reporting Limits

Parameter	Methology	Practical Quantitation Limit (PQL) Water (mg/L)	Practical Quantitation Limit (PQL) Soil (ug/g)
Arsenic	206.2/7060A/CLP	0.0050	0.50
Lead	239.2/7421	0.0050	0.50
Lead	CLP	0.0030	0.30
Lead in Drinking Water	239.2	0.0010	
Selenium	270.2/7740/CLP	0.0050	0.50
Thallium	279.2/7841/CLP	0.010	1.0

*Contract Laboratory Program (CLP) references refer to ILM04.1 and/or 6010B-CLPM (ASP 1995).

Standard Operating Procedure for Document Control

SOP No.: MET-GFAA

DISTRIBUTION LIST

DOCUMENT CONTROL No.	REVISION NUMBER	ISSUE DATE	RECIPIENT	DATE RETURNED
MET-001	0	7/14/98	M. Perry	1/18/99
~~MET-002~~	LMR 7/14/98			
MET-003	0	7/14/98	C. Kutzer	1/18/99
MET-001	1.0	1/18/99	M. Perry	8/5/99
MET-003	1.0	1/18/99	C. Kutzer	not found 11/2/01
MET-001	2.0	7/30/99	M. Perry	LMR ~~8/~~ 6/19/00
MET-003	2.0	7/30/99	C. Kutzer	11/2/01
MET-002	3.0	11/2/01	L. Reyes	
MET-003	3.0	11/2/01	C. Kutzer	

MEMO

From the QA Department

To: Department Supervisor
From: Lisa Reyes / Vicky Collom
Date:
RE: SOP Annual Review/ Newly Revised SOP

SOP for Metals Analysis by Graphite Furnace
SOP number MET-GFAA
Revision number 3
Date: 11/1/01

☐ It has been about a year since this SOP was last reviewed and it now needs to be reviewed again. Please review the SOP with your staff and complete the applicable section below.

☒ This SOP has been revised to include the changes summarized in Section 19.0. Please review this SOP with your staff and complete the section below.

☐ I have reviewed this SOP with the following personnel and it still reflects current practice.

Signature (supervisor):____________________ Date:__________

We have read, understood, and agree to perform the most recent version of this SOP or test method.

Signature	Date	Signature	Date
[signature]	11/1/01		
Tonya McCarthy	11-01-01		
[signature]	11/1/01		
Christina Kuiper	11/1/01		

☐ This SOP needs to be revised and updated to reflect current practices. This will be completed by ____________.
(date)

Signature (supervisor):____________________ Date:__________

Please indicate the outcome of your review and return this memo to me within 5 working days. Thank you for your help!!

AV

STANDARD OPERATING PROCEDURE

TOTAL SULFUR FOR ION CHROMATOGRAPHY FOR INDIANA PINES SITE

MET-ICSPINES
Revision 0
September 23, 2004

Approved By:

Supervisor	9/23/04	Date
QA Manager	9/23/04	Date
Laboratory Manager	9/23/04	Date

COLUMBIA ANALYTICAL SERVICES, INC.
1 Mustard Street, Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

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Table of Contents

Page

1. SCOPE AND APPLICABILITY

This procedure is used to determine the concentration of oxidizable sulfur in a sample using peroxide digestion and ion chromatography. This SOP describes the sample preparation step for the analysis and refers to the determinative procedure used for ion chromatography. The procedure is applicable to most sample matrices including water, wastewater, soils, and miscellaneous solids. The PQL for soils is 200 mg/Kg. This SOP was modified specifically for the Indiana Pines site project.

2. SUMMARY OF METHOD

A portion of the sample is digested using a heated peroxide solution. The resulting digestate is filtered and analyzed for sulfate using ion chromatography. The sulfate result is converted to concentration of sulfur.

3. DEFINITIONS

3.1. Laboratory Control Sample (LCS): A laboratory blank that has been fortified with target analyte and used to determine that the analysis is in control.

3.2. Matrix Spike (MS) Analysis - In the matrix spike analysis, a predetermined quantity of target analyte is added to a sample matrix prior to sample preparation and analysis. The percent recovery is calculated. The MS is used to evaluate the effects of the sample matrix on the method used for the analysis

3.3. Duplicate Sample (DUP) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4. Method Blank / Preparation Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The blank is carried through the entire analytical procedure.

3.5. Batch – Up to 20 samples of the same matrix digested together on the same day.

4. HEALTH AND SAFETY WARNINGS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical and sample should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. The laboratory maintains a compilation of Material Safety Data Sheets in binders the conference room. Always wear safety glasses or a shield for eye protection, and protective clothing, and observe proper mixing when working with these reagents.

5. CAUTIONS

Boiling samples to dryness may cause combustion

6. INTERFERENCES

Samples impervious to peroxide digestion will yield results of low bias. Samples with high organic content may require additional digestions.

7. PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8. EQUIPMENT AND SUPPLIES

8.1. 50ml Digestion Vessel for Hot Block

8.2. 250 mL glass beaker and ribbed watch glasses

8.3. Hotplate capable of maintaining a digestion temperature of 90-95°C.

8.4. Hot Block Digestor- Environmental Express

8.5. Filter Mate 2u filter paper and plunger for Environmental Express Digestion Vessel.

8.6. Dionex Ion Chromatograph Series 4000i, as described in GEN-300.0 SOP.

8.7. 10 N Sodium Hydroxide (NaOH): Dissolve 400g sodium hydroxide in distilled water, cool and dilute to 1 liter. Store at room temperature for up to 1 year.

8.8. 30% peroxide; purchased solution. Store at room temperature. Expires upon manufacturer's indications or in 1 year, whichever is sooner.

8.9. Laboratory D.I. water

8.10. Granular sodium sulfite, Na_2SO_3 anhydrous FW=126.04. 254390 mg/Kg (25.4%) sulfur. To be used for the LCS and for spiking the MS.

9. PROCEDURE

9.1. Sample Collection

9.1.1. Samples are to be collected in purchased, precleaned, certified sample containers – (plastic, glass, etc). Samples are to be cooled upon collection and shipment to lab.

9.1.2. The amount of sample collected should be 3 times the analytical aliquot, at a minimum.

9.2. Sample Handling and Preservation

9.2.1. Maintain samples at 0-6 °C upon receipt until analysis.

9.2.2. No specific holding time applies.

9.2.3. For further sample handling, storage, and custody procedures, see SMO-GEN.

9.3. Sample Preparation

9.3.1. Aqueous samples: Measure a 50 ml sample aliquot into a digestion vessel. Record the volume.

9.3.2. Soil samples: weigh out 0.5-5g of sample into a digestion vessel. Record the weight.

9.3.3. Add 2 drops of 10 N NaOH to each vessel, or until the sample is basic in nature.

9.3.4. Add appropriate standard to matrix spike and LCS aliquots.

9.3.5. Add 3 mL 30% peroxide to each vessel.

9.3.6. Bring each vessel to 50 ml with D.I. water.

9.3.7. Place digestion vessel in hotblock digester OR transfer contents of digestion vessel to a beaker and place on a hotplate.

9.3.8. Digest each sample until digestate is clear, or three times. Bring the volume of the digestate to ~ 5 - 10 mL each time taking care to not evaporate the samples to dryness. BOILING SAMPLE TO DRYNESS MAY CAUSE COMBUSTION.

9.3.9. Allow samples to cool. Bring soil and water samples to a final volume of 20.0 mL in the digestion vessel. Record the final volume. If particulates are present in the sample, filter using 2u FilterMate filter for Environmental Express digestion vessels. If one sample is filtered, the entire batch is to be filtered, including the MB and LCS.

9.3.10. Give the batch of samples and a copy of the digest sheet to Wetchem for analysis. Document custody transfer.

9.4. Sample Analysis

The extract is analyzed for sulfate by ion chromatography (IC) using SOP GEN-300. Refer to that SOP for specific analysis instructions.

9.5. Troubleshooting and Preventive Maintenance – Wipe down all hoods in the Metals Prep Lab once a week with DI water.

9.6. Data Acquisition, Calculations, and Data Reduction Requirements

9.6.1. The PeakNet software will multiply the solution result by any dilution made at the IC and by the final volume. Divide by the initial volume or weight.

9.6.2. The IC sulfate result will be multiplied by 0.3338 to obtain the concentration of the sulfur (S is 33.38% of SO_4 by atomic weight).

10. DATA AND RECORDS MANAGEMENT

10.1. **Responsibilities** – It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. **Data Flow** – Samples are entered by the Project Manager into StarLIMS v.6.11.a on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet (attached), digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using Dionex PeakNet 5 Chromatography software and the results are transferred into the StarLIMS computer system for final calculation, validation, reporting, and invoicing.

10.3. **Data Review** - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached to GEN-300) and validated by a supervisor.

11. QUALITY CONTROL AND QUALITY ASSURANCE

11.1. **Method Blank-**

11.1.1. Frequency - Prepare one method blank per batch of 20 samples.

11.1.2. Acceptance Criteria – The result of the method blank must be less than the reporting limit. If there is method blank contamination, samples which have results less than the reporting limit may be reported.

11.1.3. Corrective Action - If there is method blank contamination, attempt to find the source of the contamination, correct the problem, and re-digest the batch (with the exception of the samples accepted as above).

11.2. **LCS** –

11.2.1. Frequency – one per batch of 20 or fewer samples.

11.2.2. Acceptance criteria – The result of the LCS must be within 80-120% of the true value.

11.2.3. Corrective action – If the LCS is out of control limits, find and correct the problem and re-digest the batch.

11.3. **Matrix Spike** –

11.3.1. Frequency – one per batch of 20 or fewer samples of the same matrix.

11.3.2. Acceptance criteria – The result of the MS should be within 70-130% of the true value.

11.3.3. Corrective Action – If the MS is out of control limits, and the LCS is compliant, assume matrix interference and report. If the MS is out of control and the LCS is out of control, find the problem and redigest the batch.

11.4. IC QC Requirements are outlined in Section 12 of GEN-300.

12. REFERENCES

NELAC, 2002 Standard
CAS SOP for Ion Chromatography, GEN-300.

CAS - Rochester,NY: Total Sulfur for IC Digestion Log

Report Type: Routine // 6 // ASP // Pkg5

Analyst:________________ Date:________________

Prep Method: Total Sulfur for IC by Method 300

Digest: Initial // Redigest Of:________________

Spike Witness / Lot Approval: ________________

Batch ID: ________________

Batch Temp: ________________

	Submission / Order #	pH	Initial Vol. / Wt. (ml / g)	Final Vol(ml)	Initial Color / Clarity	Final Color / Clarity	Analyte	Spike Added Vol(ml)
1							Total Sulfur/Sulfate	
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								
25								
26								

Spiking Standards / Reagent Lot Numbers:

10 N Sodium Hydroxide (NaOH): ________________

30 % Peroxide: ________________

Sodium Sulfite (Na2SO4): ________________

Color / Clarity Key:
Color: C = Colorless ; Y = Yellow ; B = Brown ; G = Grey
BL = Black
Clarity: CDY = Cloudy ; CLR = Clear ; OP = Opaque
Texture: F = Fine ; M = Medium ; C = Coarse ; NA = Non Aqueous

COMMENTS: ________________

Metals Digestion Training Plan

Procedure:____

SOP:______________ Revision:__________ Date:________

Trainee:____________________

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated familiarity with related SOPs
   -ADM-BATCHSEQ -ADM-PCAL -ADM-SIGFIG
   -ADM-DATAENTRY -ADM-SPSR -ADM-MDL
   -ADM-TRANDOC
   Trainer:____ Trainee:____ Date:____

3. Observe performance of SOP
   -standard and reagent prep and documentation – including pipet use and balance use and calibration, if applicable
   -digestion unit set-up
   -sample prep and reagent and spike addition
   -holding times
   -benchsheet/logbook use
   -analytical sequence, batch QC required
   -time and temperature needed to digest sample, if applicable
   -preventive maintenance and other troubleshooting
   -digestate filtering and dilution
   -digestate labelling and storage

   Trainer:____ Trainee:____ Date:____

4. I have read, understood and agree to perform the most recent version of the SOP:

   Signature:________________________ Date:__________

5. Perform SOP with supervision
   - including all items in 4.
   Trainer:____ Trainee:____ Date:____

6. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.

   Trainer:____ Trainee:____ Date:____

STANDARD OPERATING PROCEDURE

DETERMINATION OF ANIONS USING ION CHROMATOGRAGPHY

GEN-300.0

Revision 3

January 19, 2004

Approved By:	______________________	__________
	Supervisor	Date
	______________________	__________
	QA Coordinator	Date
	______________________	__________
	Laboratory Manager	Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ____________

Initials: ____ Date: _____

1 SCOPE AND APPLICATION

1.1 Method 300.0 applies to the analysis of bromate, bromide, chlorate, chloride, chlorite, fluoride, nitrate-N, nitrite-N, o-phosphate-P, and sulfate by Ion Chromatography. At this time the lab routinely analyzes for only fluoride, chloride, bromide, nitrate, orthophosphate, and sulfate. The system is occasionally modified with different columns to analyze for acetate, bromate, and iodide.

1.2 Applicable Matrices

This method is defined for drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction procedure), and leachates (when no acetic acid is used).

1.3 Range

The linear range varies for the different anions. Using the settings and calibration techniques outlined in this SOP, the upper range for bromide, fluoride, nitrate and orthophosphate is 5 ppm. The upper range for chloride and sulfate is 10 ppm. Higher concentrations of anions may be determined using appropriate dilutions. Review current calibration for specific ranges.

1.4 Method Detection Limits

The method detection limits determined by 7 replicates of a known concentration, using the systems listed in Section 7 are approximately:

Analyte	Approximate MDL (mg/L)
Fluoride	0.01
Bromate	0.06
Chloride	0.06
Bromide	0.02
Nitrate-N	0.02
Orthophosphate	0.07
Sulfate	0.05
Iodide	0.2
Acetate	0.2

1.5 The PQL for the current systems are:

Analyte PQL (mg/L)

Fluoride	0.10
Bromate	0.10
Chloride	0.20
Bromide	0.10
Nitrate-N	0.05
Orthophosphate	0.10
Sulfate	0.20
Acetate	0.50
Iodide	0.40

2 METHOD SUMMARY

2.1 Sample is injected into an ion chromatograph (Dionex Series 4000i), where the anions of interest are separated and measured.

2.2 Ion chromatography is an analytical technique for the determination of all types of ions. It utilizes ion exchange mechanisms and conductivity detection for the separation and quantitation of anions or cations in a water matrix. Anions are the ion of interest for this SOP, but the theory is sound in equilibrium distribution between two different phases. The components migrate through the system only when they are in a mobile phase. The components having distributions favoring the stationary phase migrate slower than those having distributions favoring the mobile phase. Separation then results from different velocities of migration as a consequence of differences in equilibrium distributions.

2.3 The goal in any separation process is to obtain resolution, that is, the ability to separate component 1 from component 2, and is defined mathematically. No assumptions exist except that the peaks are expected to be symmetrical. Of this concept, a relationship is derived that expresses resolution as a function of three fundamental parameters in chromatographic separation, these being selectivity, efficiency, and capacity.

2.4 For our system, the mobile phase is liquid eluent (Sodium Carbonate/Bicarbonate) and the stationary phase is a polystyrene/divinylbenzene resin. The eluent controls the rate of migration through the column by its type and concentration, whereas the separation column separates anion components by their differential affinity for its stationary phase. In other words, larger size and higher charge give species more of an affinity to stay in the column. The mode of separation is High Performance Ion Chromatography utilizing a moderately low resin with a fixed ion exchange capacity of approximately 0.01-0.05 meg/g. This is the mode of choice for common inorganic ions such as F, Cl, NO3, SO4, and other polyvalent anions as well as carbohydrate analysis.

2.5 There are five major properties of IC resins used in packing HPIC columns. The properties are:

2.5.1 material
2.5.2 crosslink

2.5.3 particle size
2.5.4 functional group identity
2.5.5 capacity

2.5.6 Material base consists of polystyrene. These resins are made by copolymerizing styrene and divinylbenzene. The two functional groups react together to cross-link two polystyrene chains together making them rigid to withstand the viscous forces generated by forcing the eluent through the column.

2.5.7 The higher the cross-link, or more DVB present, the less a resin will swell in a liquid environment. Ions with larger radii will pass more easily through lower cross-linked resins.

2.5.8 Generally, the smaller the resin particle, the greater the efficiency of separation and the greater the system pressure.

2.5.9 Resins with function groups limited to the beads surface are called “pellicular” resins. Resins used in exclusion utilize “porous” resins.

2.5.10 Capacity is defined as the number of functional groups per unit volume or mass. As stated previously, common capacity for HPIC is 0.01-0.05 meq/g.

2.5.11 In addition, resins used for HPIC employ sulfonic groups covalently attached to the surface of the resin bead as a means to attach small totally porous anion exchange beads. It is these exchange particles that provide the separating capability of anions in HPIC columns. The anions separate between the mobile phase and the cationic sites.

2.5.12 The greater the valence of the sample, the greater the attraction for the ion exchange sites. Higher ionic strength eluents are needed to elute ions of the same valence, the larger the ionic radius, the more strongly they are attracted to an ion exchange site because they are more polarized. Another effect of affinity is pH. The affinity of an ion is a function of valence, and valence is a function of the pH of the eluent. Thus, pH can alter retention times of species.

2.5.13 Finally, detection is accomplished by suppressed conductivity. Conductivity is a universal property of ionic species in a solution and shows a simple dependence on concentration. By using chemical suppression, the conductivity background can be reduced to increase sensitivity and selectivity. Suppression is accomplished using an ion exchange membrane.

3 DEFINITIONS

3.1 **Independent Calibration Verification (ICV) -** ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization. The ICV is analyzed immediately following the calibration standards.

3.2 **Matrix Spike (MS**) - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for each of the analytes detected. In this method, spikes are very useful in determining proper retention times when a low concentration of an analyte is detected or expected to be adjacent to a large concentration of analyte. When a spike is used to verify retention times calculation of recovery is not necessary.

3.3 **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4 **Continuing Calibration Verification Standard (CCV) -** A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.5 **Instrument Blank (ICB/CCB) -** The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (ie. not chemically preserved). The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis. The ICB is performed once, immediately after the ICV.

3.6 **Laboratory Control Standard (LCS) -** In the LCS or blank spike analysis, predetermined quantities of standard solutions of certain analytes are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected.

4 INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems. The most common examples of this are:

4.1.1 High levels of chloride can interfere with the detection of nitrite and even nitrate.

4.1.2 Sulfite will interfere with the sulfate peak.

4.1.3 Thiosulfate can interfere if the run time of the entire chromatogram is too short.

4.2 The water dip or negative peak which elutes near fluoride can interfere with the integration of the fluoride peak. In order to account for the water dip, choose “void volume treatment” for the fluoride peak in the “data events” section of the “data processing parameters.”

5 SAFETY

Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method. All samples should be considered hazardous. Appropriate personal protective equipment including gloves, glasses, and lab coat should be worn whenever handling samples or reagents.

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1 Samples should be collected in scrupulously clean glass or polyethylene bottles. Sample handling, storage, and custody procedures are discussed in SMO-GEN.

6.2 Sample preservation and holding times used for the anions are:

Analyte	Preservation	Regular Holding Time	ASP Holding Time*
Fluoride	Cool to 0-6°C	28 days	26 days
Bromate	Cool to 0-6°C	28 days	
Bromide	Cool to 0-6°C	28 days	26 days
Chloride	Cool to 0-6°C	28 days	26 days
Nitrate-N	Cool to 0-6°C	48 hours	24 hours
O-Phosphate-P	Cool to 0-6°C	48 hours	24 hours
Sulfate	Cool to 0-6°C	28 days	26 days
Acetate	Cool to 0-6°C	28 days	
Iodide	Cool to 0-6°C	28 days	

*from VTSR (Verified Time of Sample Receipt)

7 APPARATUS AND EQUIPMENT

7.1 Analytical Balance, capable of accurately weighing to the nearest 0.0001 g.

7.2 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Dionex Ionpac AG4A-SC 4×50 mm (P/N 43175)

7.3 Anion suppressor device: Dionex anion micro membrane suppressor (P/N 53946).

7.4 Detector-Conductivity Cell: approximately 1.25 µL internal volume.

7.5 Dionex PeakNet 5.0 Chromatography Workstation software or equivalent.

7.6 Calibrated MicroPipettor and tips.

7.7 Calibrated repipettor.

7.8 IC #1

An automated sampler	(Dionex P/N 39534)
An analytical gradient pump	(Dionex System 4000i)
A separator column	(Dionex AS4A-SC 4x250mm P/N 43174)
A conductivity detector	(Dionex P/N 40157)
A 50µL sample loop	
Pump rate of 2.0 mL/min	

7.9 IC #2

An automated sampler	Model ASM-2 S/N 880113
An analytical gradient pump	Model AGP-1 S/N 921553
A separator column	Dionex AS9-HC, 4mm (or AS14 for Acetate)
A conductivity detector	Model CDM-2 S/N 921513
A degas module	Model EDM-2 S/N 930211
Sample loop	100 uL (or 50uL for acetate)
Pump rate (mL/min)	2.0 for routine / 1.0 for bromate and Iodide / 1.2 for acetate

8 PREVENTIVE MAINTENANCE

8.1 Samples that contain particles larger than 0.45 µ and reagent solutions that contain particles larger than 0.20 µ require filtration to prevent damage to instrument columns and flow systems. If there is any doubt that a sample may need filtration, filter it.

8.2 Difficult matrices such as gasoline spill samples

8.2.1 The hydrocarbons in samples of this type will "stick" to the column, which will result in a swelling of the resin and subsequent retention time shift / loss of recoveries. There is really no "threshold" of HC's below which we need not worry: the column will gradually accumulate HC's until after a few hours or days the system becomes degraded. Use the solvent compatible AS4A-SC columns, which allows cleaning out the HC contamination w/ acetonitrile, but even that will degrade the column over time.

8.2.2 Pre-treatment of the samples to remove the HC's from the water samples before injection is recommended. Dionex makes 2 sample prep cartridges which are used to remove the HC's: OnGuard RP cartridge, p/n 057084, and OnGuard P cartridge, p/n 057083.

8.2.3 Both cartridges are needed to filter one sample for each injection. Do the usual initial 1/10 dilution and then capture the filtrate after sending the first 2-3 mLs to waste.

8.3 Close eluting analytes

If a column is old and/or the resolution is poor, F can co-elute with Cl, Br with NO3. When this occurs on a calibration curve, the result is that at the high end of the curve the high standards of each anion interfere with each other, so that the individual concentrations of each anion on the curve are under-estimated (& the slope of the cal curve is low). When an individual anion, such as NO3,is run alone, without any Br in the sample, then the NO3 is then over-estimated. The same holds true for F & Cl.

Multiple scenarios can be implemented when this type of situation arises:

8.3.1 Not allowing Br and NO3 (or F & Cl) retention times to get too close on a calibration. When RT differences are less than ~0.32 minutes, and/or there is not a return to the baseline between Br & NO3, then the column should be cleaned (to remove cation contaminants which decrease resolution) or replaced with a new column.

8.3.2 Calibrate with a shorter linear range for Br. By calibrating Br to 1 ppm and NO3 to 5 ppm, the ratio of Br to NO3 at the high end is smaller, and the likelihood increases that the end of the Br peak will return to the baseline before the beginning of the NO3 peak.

8.3.3 Use an AS14 column. This Dionex column has better inherent resolution, but a longer (15-16 minute) sample time than the current AS4A-SC (between 9 & 11 minutes).

8.4 Rinsing the IC pump and valves. This should be done weekly, preferably Friday night or Saturday.

8.4.1 Disconnect the column from the valve. Plug the column with one of the solid plugs so that it doesn't dry out.

8.4.2 Attach the old column to the valve (the old column is in the IC "tool drawer" in the box on the left, behind the filters, B-cups, etc. Get the syringe then, too. It has to have the orange union fitting attached to its tip) Place the tube at the end of the column in the graduated cylinder.

8.4.3 Disconnect the eluent line, and plug it up, because it will continue to siphon all over you if you don't. Keep the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads.

8.4.4 Fill the carboy labeled "DI" about halfway with DI (rinse it once or twice first). Put the carboy back in the rack and feed the long tubing to the side of the IC. Attach the syringe to the fitting at the end of the tubing and pull the DI into the syringe to get the siphon going. When it is going, detach it from the syringe and attach it to the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads. Be sure to allow some of the water dribbling out of the DI carboy tubing to fill up any lost liquid in the brown-colored union fitting, so that you won't (hopefully) have to prime the pump.

8.4.5 Now you can turn on the pump. The DI should start flowing out the old column. Let it go for at least 15 minutes, after which time it can be turned off and you can go home.

8.4.6 As per Dionex Tech Support, this is to be done only every 6 months: While the DI is pumping through the pump & valves, lubricate the pump by opening up the pump drawer about 2 inches, exposing the pump motor housing. There is a little port in the front of the motor, with yellow grease in it. Attach the grease syringe (located in the cupboard below the IC) and squirt in 0.1 mL of grease (Dionex P/N 39440).

8.4.7 To re-configure back to operation mode:

8.4.7.1 Take off the DI carboy.

8.4.7.2 Attach the filled eluent carboy to the brown-colored union fitting after having starting the siphon, etc.

8.4.7.3 Allow the eluent to pump through the old column until you are sure that all DI has been displaced. Check with pH paper, or allow to pump >8-10 minutes.

8.4.7.4 Re-attach the valve to the guard column/analytical column.

8.5 Nightly: Release gas pressure in eluant/suppressor bottles and cap both waste ports. Fill in the daily log, recording Date, Column ID, Helium inlet pressure, System backpressure, Eluant pressure, Detector Background, and Reagent flow. Follow more detailed instruction in Section 11.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 µ.

9.2 Stock Eluent solution for IC#1: Sodium bicarbonate 1.7 mM, sodium carbonate 1.8 mM. Dissolve 11.424 g sodium bicarbonate ($NaHCO_3$) and 15.264 g of sodium carbonate (Na_2CO_3) in reagent water and dilute to 200 mL. Store at room temperature in glass or plastic for up to 1 year.

9.3 Working eluent solution for IC#1: Filter approximately 5 mLs stock eluant with 0.45µ filter. Dilute 2.5 mLs of stock eluent solution to 1L with reagent grade water. Degas for 5 minutes with Helium. This solution is stable for one week from date of preparation. Store at room temperature in plastic.

9.4 Stock Eluent solution for IC#2: Sodium Carbonate 0.5M – Dissolve 26.49g Na2CO3 in 400 mLs DI. Bring to volume in a 500 mL volumetric flask. Expires one year. Store at room temperature.

9.5 Working Eluent solution for IC#2 (AS9): Sodium Carbonate 9.0mM – Filter sufficient volume of Stock Eluent #2 through 0.45u PVDF filter cartridges. Pipet 18.0 mL filtered Stock Eluent #2 into a 1L volumetric flask and bring to volume with DI. Store at room temperature. Expires in one year.

9.6 Stock Eluent solutions for AS14 column

9.6.1 0.5 M Sodium Carbonate Concentrate– same as “Stock Eluent for IC#2”.

9.6.2 0.5M Sodium Bicarbonate Concentrate – Dissolve 21.00 g of $NaHCO_3$ in 400 mL DI. Dilute to a final volume of 500 mLs with DI. Store at room temperature. Expires in one year.

9.7 Working Eluent Solution for AS 14 Column – 3.5 mM Sodium Carbonate / 1.0 mM Sodium Bicarbonate – Pipette 7.0 mL of 0.5 M Na_2CO_3 and 2.0 mL of 0.5 M $NaHCO_3$ into a 1 Liter volumetric flask. Dilute to volume with degassed DI. Store ate room temperature. Expires in 1 week.

9.8 Regeneration solution (micro membrane suppressor): Sulfuric acid 0.1N. Dilute 5.6 mL of conc. sulfuric acid (H_2SO_4) to 2L with reagent grade water. Degas for 5 minutes with Helium. This solution is stable for one week from date of preparation. Store at room temperature in plastic.

9.9 Stock standard solutions: Stock standards are made in house or purchased commercially and expire within the vendor’s recommended expiration date or one year from receipt, whichever is sooner. Currently, the lab makes or purchases these standard solutions at 1000 mg/L for all analytes. Certificates of analysis of purchased solutions are held in the lab until the standard is no longer used and then they are archived by QA. Stocks made in the lab are from ACS reagent grade materials (dried at 103-105°C for 30 mins).

9.9.1 Bromide (Br^-) 1000 mg/L: Purchased commercially. Store at 0-6°C. Expires upon manufacturer’s indications or 1 year, whichever is sooner.

9.9.2 Bromate (BrO_3^-) 1000 mg/L: Purchased commercially. Store at 0-6°C. Expires upon manufacturer’s indications or 1 year, whichever is sooner.

9.9.3 Chloride (Cl^-) 1000 mg/L: Dissolve 1.648 g sodium chloride (NaCl) in reagent water and dilute to 1 L. Store at room temperature for up to 1 year.

9.9.4 Fluoride (F^-) 1000 mg/L Purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.9.5 Nitrate NO^-_3-N) 1000 mg/L: Dissolve 7.22 g potassium nitrate (KNO_3) in reagent water in a 1 L volumetric flask. Add 1.0 mL chloroform and dilute to 1 L with DI. Store at room temperature for up to 6 months.

9.9.6 Phosphate ($PO^{=}_4$-P) 1000 mg/L: Dissolve 4.394 g potassium phosphate (KH_2PO_4) in reagent water and dilute to 1 L. Store at 0-6°C for up to 1 year.

9.9.7 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.479 g sodium sulfate (Na_2SO_4) in reagent water and dilute to 1 L. Store at 0-6°C for up to 1 year.

9.9.8 Acetate 1000mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.9.9 Iodide 1000mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.10 Intermediate Calibration Standards –

9.10.1 Routine Intermediate Stock - Purchased at the Intermediate Stock Concentration (below) or prepare from Stock Standard Solutions. Store at 0-6°C. This solution may be made with all of these anions or bromate may be made in a separate flask and added to the standards for the IC#2. Expires in 6 months. Also used as LCS and MS Intermediate stock.

Analyte:	F	BrO3	Cl	Br	NO3	OPO4	SO4
Stock Conc (mg/L):	1000	1000	1000	1000	1000	1000	1000
mLs Stock:	10.0	2.5	20.0	4.0	10.0	10.0	20.0
Final Vol (mLs):	200.0	50.0	200.0	200.0	200.0	200.0	200.0
Int. Stock Conc (mg/L):	50.0	50.0	100.0	20.0	50.0	50.0	100.0

9.10.2 Intermediate Bromate and Iodide Stock – also used for the preparation of the LCS and MS.

Analyte:	BrO3	Iodide
Stock Conc (mg/L):	1000	1000
mLs Stock:	5.0	1.0
Final Vol (mLs):	100.0	10.0
Int. Stock Conc (mg/L):	50.0	100.0

9.10.3 Acetate – none – calibration standards prepared from stock standard

9.11 Calibration Standards

9.11.1 IC#1- Routine - prepared in 100 mL volumetric flask as follows: record the pipette ID used in the reagent prep logbook. Make fresh weekly. Store at 0-6°C.

Standard ID	mLs of Intermediate Stock	Final Volume, mLs	Final Std Conc. (mg/L) F	Cl	Br	NO3	OPO4	SO4
Std # 9	10.0	100.0	5.0	10.0	2.0	5.0	5.0	10.0
Std # 8	8.0	100.0	4.0	8.0	1.6	4.0	4.0	8.0
Std # 7	5.0	100.0	2.5	5.0	1.0	2.5	2.5	5.0
Std # 6	2.0	100.0	1.0	2.0	0.40	1.0	1.0	2.0
Std # 5	1.0	100.0	0.50	1.0	0.20	0.50	0.50	1.0
Std # 4	0.5	100.0	0.25	0.50	0.10	0.25	0.25	0.50
Std # 3	0.2	100.0	0.10	0.20	0.04	0.10	0.10	0.20
Std # 2	0.1	100.0	0.05	0.10	0.02	0.05	0.05	0.10
Std # 1	0.0	100.0	0.00	0.00	0.00	0.00	0.00	0.00

9.11.2 Calibration Standards for IC#2

Routine plus bromate

Standard ID	Anions-(no BrO3) MLs each Std	BrO3 mLs*	Final Volume mLs	F	Final Std Conc. (mg/L) BrO3	Cl	Br	NO3	OPO4	SO4
Std # 9	10.0	1.0	100	5.0	5.0	10.0	2.0	5.0	5.0	10.0
Std # 8	8.0	0.8	100	4.0	4.0	8.0	1.6	4.0	4.0	8.0
Std # 7	5.0	0.5	100	2.5	2.5	5.0	1.0	2.5	2.5	5.0
Std # 6	2.0	0.2	100	1.0	1.0	2.0	0.40	1.0	1.0	2.0
Std # 5	1.0	1.0	100	0.50	0.50	1.0	0.20	0.50	0.50	1.0
Std # 4	0.5	0.5	100	0.25	0.25	0.50	0.10	0.25	0.25	0.50
Std # 3	0.2	0.2	100	0.10	0.10	0.20	0.04	0.10	0.10	0.20
Std # 2	0.1	0.1	100	0.05	0.05	0.10	0.02	0.05	0.05	0.10
Std # 1	0.0	0.0	100	0.000	0.000	0.000	0.000	0.000	0.000	0.000

9.11.3 Bromate and Iodide

	mLs of Bromate and Iodide		Final Std Conc. (mg/L)

Standard ID	Intermediate Stock	Final Volume, mLs	BrO3	Iodide
Std # 7	10.0	100.0	5.0	10.0
Std # 6	6.0	100.0	3.0	6.0
Std # 5	4.0	100.0	2.0	4.0
Std # 4	1.0	100.0	0.5	1.0
Std # 3	0.4	100.0	0.2	0.4
Std # 2	0.2	100.0	0.1	0.2
Std # 1	0.0	100.0	0.0	0.0

9.11.4 Acetate

Standard ID	mLs of 1000 ppm Stock	Final Volume, mLs	Final Conc (mg/L)
Std # 5	1.0	100.0	10.0
Std # 4	0.5	100.0	5.0
Std # 3	1/10 of 10.0 Std	100.0	1.0
Std # 2	1/10 of 5.0 Std	100.0	0.5
Std # 1	0.0	100.0	0.0

9.12 Reference Standard Stocks: Reference stocks are made in house or purchased commercially and expire within the vendor's recommended expiration date or one year from receipt, whichever is sooner. Certificates of analysis are held in the lab until the stock is no longer used and then they are archived by QA. Stocks prepared in the lab are made from ACS reagent grade materials (dried at 103-105°C for 30 mins).

9.12.1 Fluoride (F^-) 1000 mg/L: Purchased commercially. Store at 0-6°C for up to 1 year.

9.12.2 Bromide (Br^-) 1000 mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.12.3 Chloride (Cl^-) 650 mg/L: Dissolve 1.070 g NaCl Crystals in reagent water and dilute to 1 L. Store at room temperature for up to 1 year.

9.12.4 Nitrate (NO^-_3-N) 180 mg/L: Dissolve 1.300 g KNO_3 crystals in reagent water. Add 1 mL chloroform and dilute to 1 L. Store at room temperature for up to 6 months.

9.12.5 Phosphate (OPO_4-P) 180 mg/L: Dissolve 0.7909 g KH_2PO_4 crystals in reagent water and dilute to 1 L. Store at 0-6°C for up to 1 year.

9.12.6 Sulfate (SO_{4-}) 3200 mg/L: Dissolve 5.80 g K_2SO_4 in reagent water and dilute to 1 L. Store at 0-6 °C for up to 1 year.

9.12.7 Bromate (BrO_3) 1000 mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.12.8 Iodide 1000 mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.12.9 Acetate 1000 mg/L: purchased commercially. Store at 0-6°C. Expires upon manufacturer's indications or 1 year, whichever is sooner.

9.13 The ICV/CCV is prepared as follows:

9.13.1 Routine intermediate CCV stock solution - prepared by diluting the following volumes of reference stocks for each anion in 1 liter of reagent grade water:

Anion	Stock Conc. (mg/L)	Volume Stock (mL)	Final Conc. (mg/L)	
Fluoride	1000	4.0	4.0	
Chloride	650	20.0	13.0	
Bromide	1000	2.0	2.0	
Nitrate	180	40.0	7.2	
Orthophosphate	180	40.0	7.2	
Sulfate		3200	4.0	12.8

NOTE: The CCV intermediate stock solution expires 6 months from date of preparation

9.13.1.1 The ICV/CCV for IC #1 is then prepared by diluting the CCV intermediate stock solution with equal parts water in small quantity (about 30 mLs DI and 30 mLs intermediate stock solution). The resulting concentrations are half of those of the intermediate solution. Prepare fresh when needed or at least once a week. Store at room temperature in plastic.

9.13.1.2 The ICV/CCV for IC #2 is prepared by adding 0.36 mLs of 1000 mg/L BrO3 reference stock to 50 mLs CCV Intermediate stock and bringing to 100 mLs with DI. The resulting concentrations are half of those of the intermediate solution and bromate is 3.6 mg/L. Prepare fresh when needed or at least once a week. Store at room temperature in plastic.

9.13.2 ICV/CCV for Acetate

Standard ID	mLs of 1000 ppm Stock	Final Volume, mLs	Final Conc (mg/L).
I/CCV	0.7	100.0	7.0

9.13.3 ICV/CCV for Bromate and Iodide

9.13.3.1 Intermediate ICV/CCV Solution

Analyte:	BrO3	Iodide
Stock Conc (mg/L):	1000	1000
mLs Stock:	4.0	8.0
Final Vol (mLs):	100.0	100.0
Conc (mg/L):	40.0	80.0

9.13.3.2 Final ICV/CCV Solution

10 mLs of Int. Reference Stock Solution, above, and bring to 100 mLs in a volumetric flask.

Analyte:	BrO3	Iodide
I/CCV TV's(mg/L):	4.0	8.0

9.14 LCS:

9.14.1 Routine LCS-Add 2.0 mLs of the intermediate stock solution (prepared same as the intermediate solution used for calibration standards) to DI in a 100 mL volumetric flask and bring to volume. The concentration of the LCS is 1.0 mg/L for F, NO_3 and OPO_4; 0.4 mg/L for Bromide; and 2.0 mg/L for Chloride and Sulfate. Store at room temperature in glass or plastic for up to one week.

9.14.2 LCS for Acetate

mLs of 1000 ppm Stock	Final Volume, mLs	Final Conc.mg/L
0.2	100.0	2.0

9.14.3 LCS for Bromate and Iodide

Analyte:	BrO3	Iodide
Int. Stock Conc:	50	100
mLs Int. Stock:	4.0	4.0
Final Vol:	100.0	100.0
True Value:	2.0	4.0

9.15 Matrix Spike Solutions:

9.15.1 Routine - Add 2.0 mL of the intermediate stock solution to 100 mL sample (or dilution of sample). Prepare fresh before use.

9.15.2 Acetate – same as LCS except using sample instead of DI.

9.15.3 Bromate and Iodide – same as LCS except using sample instead of DI.

9.16 Consumable materials.

9.16.1 5 mL vials with filter caps. (Dionex P/N 038141)
9.16.2 0.45µm syringe filters.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURE

11.1 Instrument preparation – choose instrument system according to analytes needed – see section 7 for system setups. Be sure there is a current MDL and IDC for the system.

11.1.1 Check eluent and regenerant levels in containers and fill to appropriate levels as necessary. Hand tighten caps of both jugs.

11.1.2 Remove plugs from the waste lines on the back of the instrument. Screw flow restrictor onto end of suppressor drain line (both lines are labeled).

11.1.3 Turn on Helium carrier gas (should be at approximately 17psi.) and compressed air (100 psi.) by turning the yellow handles to the up-down position and the small valves to either IC#1 or IC#2. These are located along the column to the left of the computer.

11.1.4 Start the Dionex Gradient pump – on the bottom right half of the instrument there is a button with stop / start indicator. Press the button to light the start indicator.

11.1.5 Turn on the Conductivity Cell. In the middle of the instrument there is a CELL off/on indicator. Press the button to light the "on" indicator. Allow the system to warm up for about an hour.

11.1.6 While the system is warming up, create the schedule of the day's run in the software according to the analytical sequence described below.

11.2 Sample Preparation

11.2.1 All sample vials and caps should be rinsed to remove any debris present from the manufacture.

11.2.2 If the water sample has no solids floating in it, is not turbid, and is otherwise clean and clear looking the sample may be placed directly in the sample vial. When in doubt filter the sample as described below. The sample vials hold approximately 5 mLs of sample with the vial cap properly installed. Sample should never be poured into the sample vial. Always pipette sample into vial. This will minimize contamination from materials used in the cap liners of sample bottles. Most samples are run at a initial dilution of 1/10 (or greater) so that the desired analytes are within the linear range of the standard curve and minimize contamination of column with metals and organics. See ADM-DIL for making dilutions.

11.2.3 If the sample appears to be or is known to be dirty or turbid the sample needs to be filtered before dilution. For most samples a 0.45µ micron filter on the end of a 10 cc pipette will filter the sample adequately. Use the Millex-HV filter, if possible, since it has been demonstrated free of the anions of interest and does not remove those anions. If other filters are to be used, first test them to see if they meet these requirements. See GEN-FILTER.

11.2.4 Soils - Place 1.0 g sample in B-Cup and dilute to 100 g with DI. Shake for 5 minutes. Filter and run as a water sample with 100 being the dilution factor for calculation purposes, and 1 being the reported dilution factor so that the detection limits are met.

11.2.5 Once the sample has been placed in the sample vial, place a vial cap in the vial and use the tool to press the cap down flush with the top of the vial.

11.2.6 The loaded vials should then be placed into cassettes according to the schedule created in compliance with the analytical sequence described below. Place the holder in the autosampler.

11.3 Calibration

11.3.1 The instruments must be calibrated when a new column is put in or when system configuration changes warrant calibration and every 6 months.

11.3.2 System calibration must have correlation coefficient of 0.995 or better. Delete outlier standards. Standards must be within 10% of their true value. Method 300.0 requires a minimum of 3 standards and a blank. If the removal of outlier standards does not bring the curve into compliance, recalibrate.

11.3.3 Immediately after an acceptable calibration has been achieved, run the ICV, ICB, and an LCS. If these are compliant, continue with samples as described in the daily analytical sequence.

11.4 Daily analytical sequence – If a calibration is not to be run, run samples in the following analytical sequence: CCV, CCB, LCS, 9 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples).

11.5 Instrument Shut Down –

11.5.1 Take the daily readings. Then turn the auto offset & cell to off and the pump to stop.

11.5.2 Turn the gas and air off to each IC individually by turning the small valve handles perpendicular to the gas flow direction.

11.5.3 Vent the eluent first, leave the cap very loose, and then ASAP vent the suppressor. (Vent the suppressor by slowly opening both jugs. The suppressor is acidic, so use care. Wear face shield and cover the jugs with a plastic bag for added protection).

11.5.4 Take the flow restrictor off of the suppressor drain line and plug both the eluent and suppressor drain lines.

11.5.5 After the last IC is shut off, turn both the gas and air yellow handles to the right.

Note: If refilling an IC for a night run, follow steps 2 & 3 only.

12 QA/QC REQUIREMENTS

12.1 Laboratory Control Standards (LCS)

12.1.1 LCS's must be run daily for all anions being tested for and once every 20 samples for the anion being tested.

12.1.2 LCS's must be within 10% of the true value.

12.1.3 If the LCS is outside the acceptance criteria stop the run, correct the problem and reanalyze the LCS. Otherwise, the samples may be reported for the anions which were in control, but not for the ones which were out of control limits. Exception: if the LCS recovery is high and sample results less than the reporting limit, analysis may continue and data may be reported.

12.2 Method Detection Limits (MDL)

MDLs should be performed every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response. The result of the MDL must be less than the PQL. If it is not, correct the problem and do another MDL study or raise the PQL. See ADM-MDL for procedure.

12.3 Initial and Continuing Calibration Verification (ICV/CCV)

12.3.1 An ICV is analyzed immediately after the standards. The ICV must be +/- 10% of the true value or the curve may not be used for anions not in control.

12.3.2 A CCV is analyzed every 10 samples.

12.3.3 All CCVs for the anions being tested for must be within 10% of the true value. NOTE: If the analyst is not looking for all 6 of the normal anions then only the values of the anions in question need be within range. If the CCV is not in control, correct the problem, obtain a compliant CCV and reanalyze all samples bound by the non-compliant CCV. Recalibrate if necessary.

12.4 Continuing Calibration Blanks (CCB)

12.4.1 A CCB must be analyzed every 10 samples immediately following the CCV.

12.4.2 All CCB's must be less than the PQL for the anion being tested. If the CCB is above the PQL, correct the problem and obtain a compliant CCB following a compliant CCV. Reanalyze samples bound by non-compliant CCB. Recalibrate if necessary.

12.5 Matrix Spikes (MS)

12.5.1 A matrix spike must be analyzed for each anion being tested. A matrix spike must be analyzed once every 10 samples for each anion being tested.

12.5.2 The matrix spike should be within the lab-generated limits in the Wetchem QC Table (found in the Quality Assurance Manual). If it is not, notify project chemist to note the outlying recovery in the case narrative or flag the associated data.

12.6 Duplicates (DUP)

12.6.1 A DUP must be analyzed every 20 samples per anion being tested. The DUP is regularly analyzed every 10 samples since the MS must be analyzed every 10 samples.

12.6.2 The acceptance criteria for a DUP is less than 20% RPD or ± the reporting limit if the sample is less than 5 times the reporting limit.

12.6.3 If a DUP is outside of the acceptance criteria, reanalyze to confirm and flag with an asterisk (estimated).

12.7 Data Acceptance

12.7.1 If the concentration of the anion is outside the working range of the instrument then a dilution should be performed. The working range is defined as the low standard concentration to the high standard concentration for the anion being tested.

12.7.2 Be sure the peaks on the chromatogram and the instrument calculated concentration make sense. Sometimes the software will attempt to integrate overrange peaks and will assign them a concentration which would be acceptable for the dilution if it was a reasonable integration.

12.7.3 On occasion, the software integrates peaks incorrectly. The sample may be reanalyzed or the analyst may use the software to correct the integration. Any manual integration or manipulation of peaks must follow the SOP for the manual integration of peaks in SOP ADM-INT.

13 DATA REDUCTION AND REPORTING

13.1 Using IC computer terminal download data into GARRS (General Chemistry Analytical Review & Reporting System).

13.1.1 In the PeakNet Main Menu, click on “Batch” icon.

13.1.2 Open file “To GARRS”

13.1.3 Click on “Input, Select.” This will pull up a list of schedules. Double click on the schedule which you want to download.

13.1.4 Click on “Export.” Name the file using date from schedule.

13.2 Using a main computer terminal, double click on the GARRS icon and click on continue for the first 5 screens.

13.2.1 Pull down “Result Uploads menu, Instrument Upload.”

13.2.2 Open the “T” drive, Double click on “Instdata, Genchem, IC, and then on the schedule you want to open.

13.2.3 Pull down “Review Report Data menu, Print General Chemistry Forms”

13.2.4 Continue. Click on EDD Standard File, Review on Screen. Click on the envelope icon and change format to text. Save in “K” drive under data transfer “Ic_xf” overwrite casedd2. Exit GARRS.

13.3 Double click on IC transfer icon. This transfers data to LIMS. QC must then be entered into LIMS manually.

13.4 Data will be reviewed by the analyst and a qualified peer using the Data Quality Checklist and validated by supervisor as outlined in ADM-DREV.

14 METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15 WASTE MANAGEMENT AND POLLUTION PREVENTION

Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.
All samples and reagents are aqueous and can be disposed of in any sink. See SMO-SPLDIS.

16 CORRECTIVE ACTION FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18 REFERENCES

18.1 Method 300.0, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R-93/100 Revised August 1993.

18.2 Method 4110 B in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.

19 TRAINING OUTLINE

19.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2 Observe Sample Preparation and Analysis. Follow items in the IC Training Plan Form.

19.3 Participate in the methodology, documentation, and data reduction with guidance.

19.4 Review Instrument Operation and Maintenance with trainer.

19.5 Demonstrate Competency by performing the analysis independently. Analyze four LCSs for an IDC. If recovery is within acceptable limits, complete Training Plan Form, summary spreadsheet and IDC Certificate and file with QA. Continuing demonstration of competency (CDC) is performed annually by an acceptable PE, single blind, or new 4 replicate study.

20 METHOD MODIFICATIONS

None

21 INSTRUMENT-SPECIFIC ADDENDUM

21.1 Each day the instrument is checked to see that working conditions are consistent. Record the actual readings in a log book on a daily basis.

21.1.1 The incoming pressure of the Helium carrier is checked (should be approx. 17 psi.)

21.1.2 The system pressure is checked (usually around 1500 psi.).

21.1.3 The background of the detector should be around 16-17 μs.

21.1.4 The flow rate of the suppressor coming from the waste line should be 5-6 mL per minute.

21.2 The instrument manuals are located next to the instrument.

22 ATTACHMENTS

None

23 CHANGES FROM PREVIOUS REVISION

- Added Acetate and Iodide throughout – including PQLs (1.5), MDLs (1.4), holding times (6.2), pump rates (7.8&7.9), columns (7.8&7.9), loopsize (7.8&7.9), eluent prep, standards prep.
- Added sections (especially in standards preparation) for analyzing Bromate and Iodide together.
- Changed the concentration of Bromide in the Intermediate and Working standards – it was lowered by a factor of 2.5 to reduce interference with close eluting analytes.
- Added reference to GEN-FILTER.
- Added to 11.1 to check the type of system needed and that there is a current MDL and IDC for the system.
- Removed requirements specific to the State of South Carolina since we no longer carry IC certification with SC.
- Added instructions for shutting down the instrument
- Expanded upon instructions for starting up the instrument

- Added discussion about close eluting analytes in Preventive Maintenance
- Added discussion about Difficult matrices and Hydrocarbon contaimation in Preventive Maintenance
- Expanded upon discussion of Rinsing the pump and valves in Preventive Maintenance.
- Updated MDLs in 1.4.
- Changed the wording in 12.6.1 to indicate a DUP is usually run 1/10 samples although it is only required 1/20.
- Changed the corrective action for a MS failure – do not need to confirm.

Addendum 6/15/04
Effective Date: 3/17/2004

The differences between the Operating Procedure of Method 300 and Method 9056 are minor. When the lab is to use Method 9056, the differences are as below.

1 SCOPE AND APPLICATION

Method 9056 applies to the analysis of bomb combustion solutions (Extraction method 5050 – See GEN-BOMB) and water samples.

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

Method 9056 holding time is “as soon as possible after collection”.

12 QA/QC REQUIREMENTS

The recovery of the opening CCV of the run must be within 10% of the true value (same as Method 300) AND the peak must be within 10% of the retention time of the CCV on the previous run. The recovery of any subsequent CCVs in the run must be within 10% of the true value AND within 5% of the opening CCV.

The frequency requirements of the MS and DUP are interchanged between Method 300 and 9056. Method 9056 requires a DUP to be run every 10 samples and a MS every 20. Method 300 requires a DUP to be run every 20 samples and a MS every 10. Regular practice is to run both a DUP and a MS every 10 samples.

13 CALCULATIONS

When analyzing samples combusted by Method 5050, the amount of bomb washings and the initial sample weight must be taken into consideration for the amount of halogens in the initial sample.

For Halogens - Determine the dilution to enter in the PeakNet software:

Multiply the final volume of the bomb washings (V_w) by the manual dilution made of the washings at the bench (D_{IC}). Divide by the initial weight of sample combusted (m). $D_f = D_{IC}V_w/m$.

For nitric and/or sulfuric acid - determined for BTU correction - use the IC result without correcting the dilution for sample weight or volume of washings. The volume of washings will be accounted for in the calculations in the BTU spreadsheet and the initial sample weight is irrelevant since the heat produced from the formation of nitric and sulfuric acid must be subtracted from the gross heat before dividing by the mass (See GEN-BOMB).

20 METHOD MODIFICATIONS

Instead of using a suppressor column and the method 9056 prescribed eluent (older technology), this lab uses suppressed conductivity and the same eluent as is used for Method 300.0 (newer technology). The samples are not matrix-matched to the eluent since this newer technology achieves desirable resolution and response without modifying the matrix.

STANDARD OPERATING PROCEDURE

DETERMINATION OF SULFUR IN SOILS USING ION CHROMATOGRAGPHY AFTER ALKALINE DIGESTION FOR INDIANA PINES SITE

GEN-300Pines

Revision 0

September 24, 2004

Approved By: ______________________ 9/24/04
Supervisor Date

______________________ 9/24/04
QA Coordinator Date

Lisa Reyes for MCP 9/24/04
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

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Table of Contents

1 SCOPE AND APPLICABILITY

1.1 This SOP uses Method 300.0 for the analysis of sulfate by Ion Chromatography in soil samples prepared by alkaline digestion according to MET-ICS.

1.2 Range

Using the settings and calibration techniques outlined in this SOP, the upper range for sulfate is 10 ppm (solution concentration). Higher concentrations of sulfate may be determined using appropriate dilutions. Review current calibration for specific ranges.

1.3 The PQL for the current system is 0.20 mg/L

2 SUMMARY OF METHOD

Sample digested by alkaline digestion. The extract is filtered and injected into an ion chromatograph (Dionex Series 4000i). Sulfate is chromatographically separated and measured with a conductivity detector. Suppression is accomplished using an ion exchange membrane. It is assumed that all of the sulfur is converted to sulfate during the digestion. The sulfate results are converted by calculation to concentration of sulfur in the original soil sample.

3 DEFINITIONS

3.1 **Initial Calibration -** analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2 **Independent Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization. The ICV is analyzed immediately following the calibration standards.

3.3 **Relative Percent Difference (RPD)** – The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.4 **Batch -** Samples processed together as a unit, not to exceed 20 investigative samples.

3.5 **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.6 **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.7 **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.7.1 **Matrix Spike (MS)** - In the matrix spike analysis, predetermined quantities of standard solutions of certain analytes are added to a sample matrix prior to analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected. In this method, spikes are very useful in determining proper retention times when a low concentration of an analyte is detected or expected to be adjacent to a large concentration of analyte. When a spike is used to verify retention time, calculation of recovery is not necessary.

3.7.2 **Duplicate Sample (DUP)** - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.7.3 **Continuing Calibration Verification Standard (CCV)** - A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7.4 **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (ie. not chemically preserved). The purpose of the ICB/CCB is to determine the levels of contamination associated with the instrumental analysis. The ICB is performed once, immediately after the ICV.

3.7.5 **Laboratory Control Standard (LCS)** - In the LCS or blank spike analysis, predetermined quantities of standard solutions of certain analytes are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected.

4 HEALTH AND SAFETY WARNINGS

- Take all appropriate safety precautions for handling reagents and samples when performing this procedure. This includes the use of personnel protective equipment, such as safety glasses, lab coat and the correct gloves.

- Handle chemicals, reagents and standards as described in the CAS safety policies, approved methods and in MSDSs where available.

- The use of pressurized gases is required for this procedure. Exercise care when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

- When releasing the cap on the suppressor reagent, wear a face shield and exercise caution. The container is pressurized and the reagent will emit a fine mist. Turn the cap slowly.

5 INTERFERENCES

5.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems. The most common examples of this are:

5.1.1 Sulfite will interfere with the sulfate peak.

5.1.2 Thiosulfate can interfere if the run time of the entire chromatogram is too short.

6 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 4-year degree (or 2-yr degree plus one year experience) in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

7 EQUIPMENT AND SUPPLIES

7.1 Analytical Balance, capable of accurately weighing to the nearest 0.0001 g.

7.2 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Dionex Ionpac AG4A-SC 4×50 mm (P/N 43175)

7.3 Anion separator column: Dionex AS14 4x250 (P/N 046124). Expires when separation between the anions of interest is no longer acceptable or upon manufacturer's indications, whichever occurs first.

7.4 Anion suppressor device: Dionex anion micro membrane suppressor (P/N 53946).

7.5 Detector-Conductivity Cell: approximately 1.25 µL internal volume.

7.6 Dionex PeakNet 5.1 Chromatography Workstation software or equivalent. Personal computer connected to network, capable of running the PeakNet software.

7.7 Calibrated MicroPipettor and tips.

7.8 Calibrated repipettor.

7.9 System configuration

An automated sampler	(Dionex P/N 39534)
An analytical gradient pump	(Dionex System 4000i)
A separator column	(Dionex AS14 4x250mm P/N 046124)
A conductivity detector	(Dionex P/N 40157)
A 50μL sample loop	
Pump rate of 2.0 mL/min	

7.10 **<u>Standards Preparation General Information</u>**

- Bring any cooled parent stocks to room temperature before use.
- All standards and reagents are to be tightly capped when not in immediate use. Protect standards and reagents from light whenever possible.

7.11 Reagent water: Distilled or deionized water, free of the anions of interest.

7.12 Stock Eluent solutions for AS14 column

7.12.1 0.5 M Sodium Carbonate Concentrate– Dissolve 26.49g Na2CO3 in 400 mLs DI. Bring to volume in a 500 mL volumetric flask. Expires one year. Store at room temperature.

7.12.2 0.5M Sodium Bicarbonate Concentrate – Dissolve 21.00 g of $NaHCO_3$ in 400 mL DI. Dilute to a final volume of 500 mLs with DI. Store at room temperature. Expires in one year.

7.13 Working Eluent Solution for AS 14 Column – 3.5 mM Sodium Carbonate / 1.0 mM Sodium Bicarbonate – Filter a sufficient volume of each of the 2 eluent reagents through 0.2 μm syringe filters into separate dispo cups. Pipette 7.0 mL of 0.5 M Na_2CO_3 and 2.0 mL of 0.5 M $NaHCO_3$ into a 2 Liter volumetric flask. Dilute to volume with DI. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. Store at room temperature. Expires in 1 week.

7.14 Regeneration solution (micro membrane suppressor): Sulfuric acid 0.1N. Dilute 5.6 mL of conc. sulfuric acid (H_2SO_4) to 2L with reagent grade water. Degas for 5 minutes with ultra high purity Helium at a rate of 1-5 bubbles per second. This solution is stable for one week from date of preparation. Store at room temperature in plastic.

7.15 Stock standard solutions

7.15.1 Sodium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.15.2 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.479 g prepared (as above) sodium sulfate (Na_2SO_4) in reagent water and dilute to 1 L. Store at 0-6°C in amber glass for up to 1 year.

7.16 Intermediate Calibration Standards –

7.16.1 Routine Intermediate Stock – Store at 0-6°C in plastic. Expires in 6 months. Also used as LCS and MS Intermediate stock.

Analyte:	SO_4
Stock Conc (mg/L):	1000
mLs Stock:	20.0
Final Vol (mLs):	200.0
Int. Stock Conc (mg/L):	100.0

7.17 Calibration Standards - prepared in 100 mL volumetric flask as follows: record the pipette ID used in the reagent prep logbook. Make fresh weekly. Store at 0-6°C in glass or plastic.

Standard ID	mLs of Intermediate Stock	Final Volume, mLs	Working conc. SO_4 mg/L
Std # 9	10.0	100.0	10.0
Std # 8	8.0	100.0	8.0
Std # 7	5.0	100.0	5.0
Std # 6	2.0	100.0	2.0
Std # 5	1.0	100.0	1.0
Std # 4	0.5	100.0	0.50
Std # 3	0.2	100.0	0.20
Std # 2	0.1	100.0	0.10
Std # 1	0.0	100.0	0.00

7.18 Reference Standard Stocks:

7.18.1 Potassium Sulfate – ACS reagent grade dried at 103-105°C for 30 mins. Store dried material in a small glass beaker. Enclose the beaker in aluminum foil to protect from light. Store the covered beaker in a desiccator. Expires in one year.

7.18.2 Sulfate (SO_4.) 3200 mg/L: Dissolve 5.80g dried (as above) K_2SO_4 in reagent water and dilute to 1 L. Store at 0-6 °C in amber glass for up to 1 year.

7.19 ICV/CCV Intermediate stock (12.8 mg/L) - Dilute 4.0 mL of 3200 mg/L reference stock to 1 Liter in a volumetric flask. Store at 0-6°C in plastic for up to 6 months.

7.20 ICV/CCV (6.4 mg/L) - prepare by diluting the CCV intermediate stock solution with equal parts water in small quantity (about 30 mLs DI and 30 mLs intermediate stock solution). The resulting concentrations are half of those of the intermediate solution. Prepare fresh when needed or at least once a week. Store at room temperature in plastic.

7.21 LCS (2.0 mg/L): Store at room temperature in glass or plastic for up to one week. Add 2.0 mLs of the intermediate stock solution (prepared same as the intermediate solution used for calibration standards) to DI in a 100 mL volumetric flask and bring to volume.

7.22 Matrix Spike Solution - Add 2.0 mL of the intermediate stock solution to 100 mL sample (or dilution of sample). Prepare fresh before use.

7.23 Consumable materials.

- 5 mL vials with filter caps. (Dionex P/N 038141)
- 0.2 µm syringe filters.

8 PROCEDURE

8.1 Calibration and Standardization-

8.1.1 Prepare calibration standards according to Section 7. Document preparation in standards log book. Load standards according to Autosampler Vial Loading Section. Start instrument and analyze according to sections below.

8.1.2 The initial calibration is made by linear regression. This method of quantitation uses the equation of a line ($y=mx+b$). The curve <u>must not</u> be forced through zero. System calibration must have correlation coefficient of 0.995 or better. Delete outlier standards. Standards must be within 10% of their true value. Method 300.0 requires a minimum of 3 standards and a blank. If the removal of outlier standards does not bring the curve into compliance, recalibrate.

8.1.3 Immediately after an acceptable calibration has been achieved, run the ICV, ICB, and an LCS. If these are compliant, continue with samples as described in the daily analytical sequence.

8.2 **Sample Collection** – Samples should be collected in purchased, certified clean glass or polyethylene bottles or jars.

8.3 Sample Handling and Preservation – Sulfate holding time is 28 days from collection. Samples stored at 0-6°C from receipt until analysis. Sample handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

8.4 Sample Preparation – Soil samples for Total Sulfur are digested according to MET-ICS. Further preparation of the extract is given below.

8.5 Sample Analysis –

8.5.1 **Prepare the Instrument** –

8.5.1.1 Be sure there is a current MDL and IDC for the system.

8.5.1.2 Check eluent and regenerant levels in containers. Fill to appropriate levels as necessary. Hand tighten caps of both jugs.

8.5.1.3 Remove plugs from the waste lines on the back of the instrument. Screw flow restrictor onto end of suppressor drain line (both lines are labeled).

8.5.1.4 Turn on Helium carrier gas (should be at approximately 17psi.) and compressed air (100 psi.) by turning the yellow handles to the up-down position and the small valves to IC#1. These are located along the column to the left of the computer.

8.5.1.5 Start the Dionex Gradient pump – on the bottom right half of the instrument there is a button with stop / start indicator. Press the button to light the start indicator.

8.5.1.6 Turn on the Conductivity Cell. In the middle of the instrument there is a CELL off/on indicator. Press the button to light the "on" indicator. Allow the system to warm up for about an hour.

8.5.2 Create a schedule in the PeakNet software -

8.5.2.1 While the system is warming up, determine whether an ICAL is to be run. The instruments must be calibrated if any of the following apply:

- when a new column is put in
- when system configuration changes warrant calibration
- every 6 months
- when QC samples indicate the old calibration is no longer acceptable.

8.5.2.2 Determine which samples are to be analyzed.

8.5.2.3 Remove any standards or reagents needed from the cooler and allow to warm to room temperature before use.

8.5.2.4 Create the schedule of the day's run in the software. This may be modified later as needed, but will help with initial organization.

8.5.2.5 If a calibration is not to be run – set up the schedule to analyze samples in the following analytical sequence: CCV, CCB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Skip the initial calibration section. Prepare the samples and load the autosampler as described below.

8.5.2.6 If a calibration is to be run – set up the schedule to analyze the calibration standards, ICV, ICB, LCS, 10 samples, CCV, CCB, 10 samples, CCV, CCB, LCS, etc. with a CCV/CCB set after every 10 samples and an LCS after every 20 samples and DUP/MS where appropriate (at no particular position but one set for every 10 samples). Continue with initial calibration section.

8.5.3 **Prepare the extract for analysis**–

8.5.3.1 Draw the extract up into a 10 mL pipette. Place a 0.2 µm syringe filter on the end of the pipette and push some of the sample (only enough to make a dilution – 2 mLs is plenty) through the filter into a dispo cup.

8.5.3.2 Use the filtered extract to make an appropriate dilution.

8.5.4 Autosampler Vial Loading

8.5.4.1 Rinse all sample vials and caps to remove any debris present from the manufacture.

8.5.4.2 Once the sample or standard has been placed in the sample vial, place a vial cap in the vial and use the tool to press the cap down flush with the top of the vial.

8.5.4.3 Place the loaded vials into cassettes according to the schedule created and in compliance with the analytical sequence described below. Place the holder in the autosampler.

8.5.5 Start Instrumental Analysis

8.5.5.1 Open the run screen in the PeakNet software. Load the schedule. Select Start.

8.5.5.2 Push the "auto off-set" button on the IC unit to reset the conductivity baseline.

8.5.5.3 Press "Run" on the autosampler.

8.5.6 Evaluate sample analysis

8.5.6.1 Examine solution concentrations of target analytes in the samples. If the concentration is greater than the high calibration standard, reanalyze the sample at a dilution.

8.5.6.2 Check peak integrations.

8.5.6.2.1 Where possible, all integrations should be performed consistent with integration of the corresponding calibration standards.

8.5.6.2.2 Be sure the peaks on the chromatogram and the instrument calculated concentration make sense. Sometimes the software will attempt to integrate overrange peaks and will incorrectly assign them a concentration which would be acceptable for the dilution if it was a reasonable integration.

8.5.6.2.3 On occasion, the software integrates peaks incorrectly. The sample may be reanalyzed or the analyst may use the software to correct the integration. Any manual integration or manipulation of peaks must be consistent with the calibration standards and the QC samples.

8.5.6.3 Evaluate QC samples. All samples must be bracketed by acceptable CCVs and CCBs. See Section 10 for further discussion of QC and sample acceptance and corrective action.

8.5.7 **Instrument Shut Down** –

8.5.7.1 Take the daily readings. Then turn the auto offset & cell to off and the pump to stop.

8.5.7.2 Turn the gas and air off to each IC individually by turning the small valve handles perpendicular to the gas flow direction.

8.5.7.3 Vent the eluent first, leave the cap very loose, and then ASAP vent the suppressor. (Vent the suppressor by slowly opening both jugs. The suppressor is acidic, so use care. Wear face shield and cover the jugs with a plastic bag for added protection).

8.5.7.4 Take the flow restrictor off of the suppressor drain line and plug both the eluent and suppressor drain lines.

8.5.7.5 After the last IC is shut off, turn both the gas and air yellow handles to the right.

8.6 Troubleshooting –

8.6.1 Rinsing the IC pump and valves. This should be done weekly, preferably Friday night or Saturday.

8.6.1.1 Disconnect the column from the valve. Plug the column with one of the solid plugs so that it doesn't dry out.

8.6.1.2 Attach the old column to the valve (the old column is in the IC "tool drawer" in the box on the left, behind the filters, B-cups, etc. Get the syringe then, too. It has to have the orange union fitting attached to its tip) Place the tube at the end of the column in the graduated cylinder.

8.6.1.3 Disconnect the eluent line, and plug it up, because it will continue to siphon all over you if you don't. Keep the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads.

8.6.1.4 Fill the carboy labeled "DI" about halfway with DI (rinse it once or twice first). Put the carboy back in the rack and feed the long tubing to the side of the IC. Attach the syringe to the fitting at the end of the tubing and pull the DI into the syringe to get the siphon going. When it is going, detach it from the syringe and attach it to the brown-colored union fitting attached to the blue-colored tubing that leads to the pump heads. Be sure to allow some of the water dribbling out of the DI carboy tubing to fill up any lost liquid in the brown-colored union fitting, so that you won't (hopefully) have to prime the pump.

8.6.1.5 Now you can turn on the pump. The DI should start flowing out the old column. Let it go for at least 15 minutes, after which time it can be turned off and you can go home.

8.6.1.6 As per Dionex Tech Support, this is to be done only every 6 months: While the DI is pumping through the pump & valves, lubricate the pump by opening up the pump drawer about 2 inches, exposing the pump motor housing. There is a little port in the front of the motor, with yellow grease in it. Attach the grease syringe (located in the cupboard below the IC) and squirt in 0.1 mL of grease (Dionex P/N 39440).

8.6.2 To re-configure back to operation mode:

8.6.2.1 Take off the DI carboy.

8.6.2.2 Attach the filled eluent carboy to the brown-colored union fitting after having starting the siphon, etc.

8.6.2.3 Allow the eluent to pump through the old column until you are sure that all DI has been displaced. Check with pH paper, or allow to pump >8-10 minutes.

8.6.2.4 Re-attach the valve to the guard column/analytical column.

8.6.3 Nightly: Release gas pressure in eluant/suppressor bottles and cap both waste ports. Fill in the daily log, recording Date, Column ID, Helium inlet pressure, System backpressure, Eluant pressure, Detector Background, and Reagent flow.

8.6.3.1 The incoming pressure of the Helium carrier is checked (should be approx. 17 psi.)

8.6.3.2 The system pressure is checked (usually around 1500 psi.).

8.6.3.3 The background of the detector should be around 22-24 μs.

8.6.3.4 The flow rate of the suppressor coming from the waste line should be 3-4 mL per minute.

8.6.4 Maintenance log – Document all preventive maintenance, as well as instrument repair, in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.7 Data Acquisition, Calculations, and Data Reduction Requirements

8.7.1 The results which are printed on the instrument report will be adjusted for any dilution made at the instrument. Further adjustment for initial weight and final volume will be made separately. The final multiplication by 0.3338 (sulfur is 33.38% of sulfate by molecular weight) will be done by StarLIMS.

8.7.2 Data will be reviewed by the analyst and a qualified peer using the Data Quality Checklist (attached) and validated by supervisor.

8.7.3 All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report

8.8 Computer Hardware and Software

8.8.1 StarLIMS v.6.11.a
8.8.2 Personal Computer running Dionex PeakNet v5.1

9 DATA AND RECORDS MANAGEMENT

9.1 **Responsibilities** - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

9.2 **Data Flow** – Samples are entered by the Project Manager into StarLIMS on a Personal Computer running on a Novell Network. On the day that the samples are received the samples appear on a daily log printed from this computer system. The Metals Prep analyst prepares a benchsheet, digests the samples and turns the samples and digest sheet over to the IC analyst. The samples are analyzed for sulfate using PeakNet software. The results are printed and hand entered into StarLIMS. StarLIMS makes the final calculations and the results are printed for data review. When the results are approved, the StarLIMS is used for reporting, and invoicing.

9.3 **Data Review** - Data will be reviewed by the IC analyst and a qualified peer using a Data Review Checklist (attached) and validated by a supervisor.

10 QA/QC REQUIREMENTS

10.1 Laboratory Control Standards (LCS)

10.1.1 An LCS must be run daily and once every 20 samples.

10.1.2 The LCS must be within 10% of the true value.

10.1.3 If the LCS is outside the acceptance criteria stop the run, correct the problem and reanalyze the LCS. Exception: if the LCS recovery is high and sample results less than the reporting limit, analysis may continue and data may be reported.

10.2 Method Detection Limits (MDL)

MDLs should be performed every 6 months, when a new operator begins work or whenever there is a significant change in the background or instrument response. The result of the MDL must be less than the PQL. If it is not, correct the problem and do another MDL study or raise the PQL. See 40 CFR Part 136 Appendix B.

10.3 Initial and Continuing Calibration Verification (ICV/CCV)

10.3.1 An ICV is analyzed immediately after the standards. The ICV must be 90-110% of the true value or the curve may not be used.

10.3.2 A CCV is analyzed every 10 samples.

10.3.3 All CCVs must be within 10% of the true value. If the CCV is not in control, correct the problem, obtain a compliant CCV and reanalyze all samples bound by the non-compliant CCV. Recalibrate if necessary. Exception: if the CCV recovery is high and sample results are less than the reporting limit, analysis may continue and data may be reported.

10.4 Continuing Calibration Blanks (CCB)

10.4.1 A CCB must be analyzed every 10 samples immediately following the CCV.

10.4.2 All CCB's must be less than the PQL. If the CCB is above the PQL, correct the problem and obtain a compliant CCB following a compliant CCV. Reanalyze samples bound by non-compliant CCB. Recalibrate if necessary. Exception: If there is blank contamination and the sample results are less than the reporting limit, analysis may continue and data may be reported.

10.5 Matrix Spikes (MS)

10.5.1 A matrix spike must be analyzed once every 10 samples. Do not choose field blanks for the analysis of MS.

10.5.2 The matrix spike should be within the lab-generated limits of 69-120% for waters and 70-130 % for soils. If it is not, note the outlying recovery in the case narrative. If the MS is out and the LCS is in, matrix interference is assumed and the batch is acceptable. It is recommended that the MS be reanalyzed to confirm the outliers, however it is not required.

10.6 Duplicates (DUP)

10.6.1 A DUP must be analyzed every 20 samples. The DUP is regularly analyzed every 10 samples since the MS must be analyzed every 10 samples. Do not choose field blanks for analysis of DUP.

10.6.2 The acceptance criteria for a DUP is less than 20% RPD or ± the reporting limit if the sample is less than 5 times the reporting limit.

10.6.3 If a DUP is outside of the acceptance criteria, reanalyze to confirm and flag with an asterisk (estimated).

11 REFERENCES

- Method 300.0, *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R-93/100 Revised August 1993.
- Method 4110 B in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.
- NELAC 2002 Standard
- 40CFR Part 136 Appendix B

Ion Chromatography Analysis Training Plan

Procedure:____

SOP:____________ Revision:________ Date:_______

Trainee:__________________

1. Read SOP Trainer:____ Trainee:____ Date:____

2. Demonstrated understanding of the scientific basis of the analysis including:
   -column separation, retention time
   -supressor and eluent functions
   -method of detection
   -Correlation co-efficients and results based on calculated curves
   Trainer:____ Trainee:____ Date:____

3. Demonstrated familiarity with related SOPs
   -ADM-BATCHSEQ -ADM-PCAL -ADM-SIGFIG
   -ADM-DATAENTRY -ADM-DIL -ADM-SPSR
   -ADM-MDL -ADM-DREV -ADM-TRANDOC
   Trainer:____ Trainee:____ Date:____

4. Observe performance of SOP
   -sample preparation (soil, water, other matrices)
   -standard and reagent prep and documentation – including pipet(s) used
   -IC start-up and warm-up procedures
   -software use, entering sample IDs in analytical sequence
   -sample dilution guidelines (1/10 or more unless F, OPO4; 1/50 or more for leachates; other nasties; use of historical data)
   -holding times
   -use and loading of vials (filter if necessary, no air in tubes)
   -use and loading of autosampler
   -sample analysis including:
     -calibration
     -software command of instrument
     -recognition of normal vs. abnormal peaks
       -linear range
       -manual integration
     -use of QC samples and QC criteria
   -IC instrument logbook use
   -data reduction, reporting, and review
   Trainer:____ Trainee:____ Date:____

5. I have read, understood and agree to perform the most recent version of the SOP:

   Signature:______________________ Date:_________

6. Perform SOP with supervision
   - including all items in 4.
   Trainer:____ Trainee:____ Date:____

7. Independent performance of the SOP
   -all of the item listed in 4
   -IDC (4 mid-range standards performed before client samples are analyzed)
   -attach IDC certificate, raw data, and summary spreadsheet.
   Trainer:____ Trainee:____ Date:____

Columbia Analytical Services Inc.
An Employee-Owned Company

WET CHEMISTRY
DATA QUALITY CHECKLIST

Analysis:______________________________

Date: ____________________

Yes	No	NA				Yes	No	NA
☐	☐	☐	1.	**Holding Times** met method requirements?	1.	☐	☐	☐
☐	☐	☐	2.	**ICAL** met method requirements?	2.	☐	☐	☐
☐	☐	☐	3.	**ICV** acceptable?	3.	☐	☐	☐
☐	☐	☐	4.	**CCVs** acceptable? Analyzed per 10 samples?	4.	☐	☐	☐
☐	☐	☐	5.	**CCBs** acceptable? Analyzed per 10 samples?	5.	☐	☐	☐
☐	☐	☐	6.	**Method Blank** results <RL?	6.	☐	☐	☐
☐	☐	☐	7.	**LCS** recoveries within QC limits?	7.	☐	☐	☐
☐	☐	☐	8.	All reported sample **concentrations within LR**?	8.	☐	☐	☐
☐	☐	☐	9.	**MS** recoveries within QC limits?	9.	☐	☐	☐
☐	☐	☐	10.	**Duplicate** RPD within QC limits?	10.	☐	☐	☐
☐	☐	☐	11.	**Dilution factors** verified and calculated correctly?	11.	☐	☐	☐
☐	☐	☐	12.	**Bench Sheet** complete, initials, date, and time:	12.	☐	☐	☐
☐	☐	☐		•Are standards and reagents **traceable**?		☐	☐	☐
☐	☐	☐		•Is **unused space** on the sheet crossed out?		☐	☐	☐
☐	☐	☐		•**Pipette ID** referenced?		☐	☐	☐
☐	☐	☐	13.	**All applicable Log Books** filled in?				
			14.	**Manual data entry to LIMS correct? Date? Time?**	14.	☐	☐	☐

Analyst:________________ Peer Review:________________

Date:________________ Date:________________

COMMENTS:
****Comments must be provided for any items noted above as "No"**

STANDARD OPERATING PROCEDURE

TOTAL HARDNESS BY CALCULATION

GEN-2340B
Revision 0
January 19, 2005

Approved By: ______________________ 1/19/05
Supervisor Date

______________________ 1/19/05
QA Coordinator Date

______________________ 1/19/05
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.

Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

1 SCOPE

This SOP uses Standard Methods 2340B for the determination of Total Hardness by calculation from separate determinations of calcium and magnesium. This method is applicable to drinking, surface, and saline water, domestic and industrial wastes.

2 SUMMARY

The purpose of this procedure is to define the sum of calcium and magnesium concentrations, both expressed as mg/L calcium carbonate, in a water sample. Originally, hardness was defined as the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Hardness by calculation is based upon mineral analysis of calcium and magnesium using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP) technology and yields high accuracy, however for a more rapid result, total hardness may be determined by titration (See GEN-130.2).

3 DEFINITIONS

3.1 Total Hardness – the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

3.2 See Analytical SOP, MET-200.7/6010B for definitions pertaining to the analysis of calcium and magnesium.

4 INTERFERENCES

4.1 See Analytical SOP, MET-200.7/6010B for interferences pertaining to the analysis of calcium and magnesium.

5 SAFETY

5.1 Always wear gloves, lab coat, and safety glasses when handling samples or performing the analysis.

6 SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 Samples should be collected in purchased, certified clean glass or plastic, preserved with HNO_3 to pH<2, and stored at 0-6°C until analysis. Holding time is 6 months from date of sample collection.

6.2 Further sample handling, storage, and custody procedures are discussed in SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 See Analytical SOP, MET-200.7/6010B for equipment pertaining to the analysis of calcium and magnesium.

8 PREVENTIVE MAINTENANCE

8.1 See Analytical SOP, MET-200.7/6010B for preventive maintenance pertaining to the analysis of calcium and magnesium.

9 REAGENTS AND STANDARDS

9.1 See Analytical SOP, MET-200.7/6010B for reagents and standards pertaining to the analysis of calcium and magnesium.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURE

11.1 See Analytical SOP, MET-200.7/6010B for the procedure for the analysis of calcium and magnesium.

11.2 Calculate hardness as described in Section 13.

12 QA/QC REQUIREMENTS

12.1 See Analytical SOP, MET-200.7/6010B for QC requirements for the analysis of calcium and magnesium.

13 DATA REDUCTION AND REPORTING

13.1 Calculation:

$$\textit{Hardness, mg / L } CaCO_3 = 2.497[\text{Ca, mg/L}] + 4.118[\text{Mg, mg/L}]$$

Where: Calcium (Ca) and Magnesium (Mg) concentrations are determined by ICP analysis.

13.2 Reporting Limit = 5 mg/L.

13.3 Raw data in the laboratory pertains to the ICP analysis of calcium and magnesium. The LIMs system shall do the calculation.

13.4 Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

- See Analytical SOP, MET-200.7/6010B for the method performance for the analysis of calcium and magnesium.

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

- See Analytical SOP, MET-200.7/6010B for the waste management and pollution prevention for the analysis of calcium and magnesium.

16. CORRECTIVE ACTION FOR OUT of CONTROL DATA

- If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of SOP, MET-200.7/6010B and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT of CONTROL OR UNACCEPTABLE DATA

- If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

Method 2340 B, pp 2-36, *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.

19. TRAINING OUTLINE

13.5 See Analytical SOP, MET-200.7/6010B for the Training Outline for the analysis of calcium and magnesium.

20. METHOD MODIFICATIONS

None.

21. INSTRUMENT ADDENDUM

See Analytical SOP, MET-200.7/6010B.

22. ATTACHMENTS

None.

23. CHANGES FROM PREVIOUS REVISION

Not Applicable.

STANDARD OPERATING PROCEDURE**Error! Bookmark not defined.**

DETERMINATION OF SURFACTANTS
OR
METHYLENE BLUE ACTIVE SUBSTANCES (MBAS)

GEN –425.1
Revision 3
January 11, 2005

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL
NUMBER: ________________
Initials: ______ Date: _________

1. SCOPE AND APPLICATION

1.1. This SOP uses EPA method 425.1 for the analysis of surfactants and MBAS (Methylene Blue Active Substances) in drinking waters, surface waters, wastewaters, and wastes. This method is not applicable to soils or saline waters.

1.2. Analytes: Anionic surfactants are among the most prominent of many substances, natural and synthetic, showing methylene blue activity. The MBAS method is useful for estimating anionic surfactant content, but the possible presence of other types of MBAS must be considered. Using this method, it is not possible to differentiate between linear alkyl sulfonate (LAS) and alkyl benzene sulfonate (ABS) or other isomers of these compounds. However, LAS has essentially replaced ABS in the surfactant market.

1.3. Range: This method suggests a 250 mL sample aliquot that results in a working range of 0.04 - 0.40 mg/L MBAS. This range can be extended downward to 0.020 mg/L with a 500 mL sample and expanded upwards with dilutions.

2. METHOD SUMMARY

2.1. This method is based upon the ability of methylene blue active substances (MBAS), most notably anionic surfactants, to transfer a cationic dye (methylene blue) by ion pair formation that is strongly hydrophobic into an immiscible organic liquid (chloroform, $CHCl_3$). The blue color intensity produced in the organic phase is relative to the concentration of MBAS.

2.2. The method requires the aqueous sample to be mixed with an excess of an acidified aqueous solution of methylene blue chloride. The resulting hydrophobic ion pair is transferred by three successive extractions into chloroform. This is followed by an aqueous backwash with an acidic solution to remove the lesser hydrophobic ion pairs that can be formed by interfering substances. The chloroform layer retains the strongly hydrophobic methylene blue-anionic surface active substance ion pairs. Measurement of the blue color in the chloroform by spectrophotometry at 652 nm is related to the concentration of MBAS as determined against standards utilizing LAS.

3. DEFINITIONS

3.1. **MBAS** (methylene blue active substances) - anionic type surface substances that are active toward the cationic dye, methylene dye.

3.2. **Surfactant** - A chemical that combines in a single molecule a strongly hydrophobic group with a strongly hydrophilic one. These molecules tend to congregate at the interfaces between the aqueous medium and other phases such as air, oils, and solids. This imparts properties of foaming, emulsification, and particle suspension.

3.2.1. The hydrophobic group is generally a hydrocarbon radical (R).

3.2.2. The hydrophilic group can be of two types: ionic and nonionic.

3.2.3. The ionic hydrophilic group can be anionic or cationic and is determined by which ion remains associated with the hydrophobic group when dissociated (i.e., anionic surfactant $(RSO_3)^-Na^+$, cationic surfactant $(RMe_3N)^+Cl^-$.)

3.3. **Initial Calibration -** analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.4. **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.4.1. **Duplicate Sample (DUP) -** A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4.2. **Method Blank/ Prep Blank -** The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.4.3. **Blank Spike (LCS) -** In the blank spike analysis, a predetermined quantity of standard solution is added to a blank prior to sample extraction and analysis. Percent recoveries are calculated for the analyte detected.

3.5. **Relative Percent Difference (RPD) –** The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.6. **Batch -** Samples processed together as a unit, not to exceed 20 investigative samples. See ADM-BATCH for further discussion.

3.7. **Independent (or Initial) Calibration Verification (ICV) -** A standard from a different source as the calibration standards used to verify the calibration curve.

3.8. **Continuing Calibration Verification (CCV) -** CCV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.9. **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.10. **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

4. INTERFERENCES

4.1. Positive interferences may occur from any other anionic surface active substances that may be present. These include organic sulfonates, sulfates, carboxylates, and phenols, as well as inorganic thiocyanates, cyanates, nitrates, and chlorides. These are essentially eliminated by the backwash procedure with the exception of chlorides at the levels present in saline waters.

4.2. Negative Interferences

4.2.1. Negative interferences can result from the presence of other cationic materials (amines) that will compete with methylene blue in ion pair formation.

4.2.2. Negative results can occur from the adsorption of MBAS onto containers, glassware, and particulate material that may settle or be filtered out.

4.2.3. Sulfides, often present in raw or primary treated wastewater, may react with methylene blue to form a colorless reduction product. Eliminate this interference by prior oxidation with H_2O_2.

5. SAFETY

- Perform the extraction in a fume hood.

- All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

- Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

- Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

- Sulfuric Acid is used in this method. This acid is extremely corrosive and care must be taken while handling it. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

6. SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1. Samples are collected in purchased, certified clean plastic or glass.

6.2. The preferred volume is one liter to allow for duplicate and matrix spike analyses.

6.3. Samples should be stored at 0-6°C with no chemical preservative.

6.4. The holding time for analysis is 48 hours due to the biodegradability of LAS. The ASP holding time is 24 hours from VTSR (Verified Time of Sample Receipt).

6.5. Sample handling, storage, and custody procedures are discussed in SOP SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. Spectrophotometer for use at 652 nm.

7.2. Glassware

7.2.1. Separatory funnels - 1000 mL and 250 mL with TFE stopcocks and stoppers.

7.2.2. Funnels

7.2.3. 100 mL volumetric flasks previously dried in an oven and cooled in a desiccator.

7.3. Glass wool.

7.4. Ring weights

7.5. Vent Hood

8. PREVENTIVE MAINTENANCE

8.1. Clean glassware according to GEN-GC. Do not use soap. Keep separatory funnels for this method separate from glassware for general use.

8.2. Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.3. Have the spectrophotomer calibrated every 6 months.

9. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1. <u>Standards Preparation General Information and Disclaimers</u>

- All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 ppb standard may be made by adding 1 uL of 200 ppb to 10 mLs or may be made by adding 4 uL of 50 ppb to 10 mLs. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

- The initial calibration curves given are typical, but also subject to variation due to detection levels needed. The lowest concentration level shall be at the method reporting level. The remaining levels should define the working linear range of the analytical system.

- All Standards must be traceable using the CAS lot system (ADM-DATANTRY). Protect all standards from light.

9.2. LAS Solutions

9.2.1. LAS Standard Stock (1000 mg/L): This commercial preparation is made from Linear Alkylbenzenesulfonic Acid (molecular weight is available on certificate of analysis) in DI and preserved in 1% (v/v) H2SO4. Store at 0-6 °C. Expires per manufacturer's indications.

9.2.2. LAS Standard working stock (1.0 mg/L): Dilute 1.0 mL of 1000 mg/L LAS stock to 1000 mL D.I. water. Store at 0-6 °C for up to 1 year in amber glass.

9.2.3. LAS Reference Stock (1000 mg/L): Purchased and stored exactly the same as LAS Standard Stock except use a different lot #. Store at 0-6 °C. Expires per manufacturer's indications.

9.2.4. LAS Reference working stock (1.0 mg/L): Dilute 1.0 mL of 1000 mg/L Reference Stock to 1000 mLs with DI. Prepare fresh on day of analysis.

9.3. Phenolphthalein indicator solution, alcoholic: Dissolve 5 g phenolphthalein in 500 mL of 95% isopropanol and add 500 mL DI. Store at room temperature in plastic bottle for up to 1 year.

9.4. Isopropanol - purchased commercially. Store at room temperature in a flammable cabinet. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.5. Phenolphthalein – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.6. Sodium Hydroxide, NaOH, 50% solution - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.7. Sodium Hydroxide, NaOH, 1 N: Slowly add 80 mL of 50% NaOH solution to 800 mL DI in a 1 L volumetric flask while swirling. Dilute to 1 L. Store at room temperature in plastic bottle for up to 1 year.

9.8. Sulfuric Acid, H_2SO_4 – concentrated - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.9. Sulfuric Acid, H_2SO_4, 1 N: Slowly add 27.8 mL of concentrated sulfuric acid to 800 mL DI in a 1L volumetric flask. Bring to volume with DI. Store at room temperature in plastic bottle for up to 1 year.

9.10. Sulfuric Acid, H_2SO_4, 6 N: Slowly add 167 mL of concentrated sulfuric acid to 800 mL DI in a 1L volumetric flask. Bring to volume with DI. Expires in 1 year.

9.11. Chloroform, $CHCl_3$, purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.12. Methylene blue chloride ($C_{16}H_{18}ClN_3S \bullet 3H_2O$) - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.13. Sodium phosphate, monobasic, monohydrate ($NaH_2PO_4 \bullet H_2O$) purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.14. Methylene blue reagent: Dissolve 100 mg methylene blue chloride in 100 mL D.I. water. Transfer 30 mL to 1 L volumetric, add about 500 mL D.I. water, 41 mL 6 N H_2SO_4 and 50 g $NaH_2PO_4 \bullet H_2O$. Shake until dissolved and make up to volume with D.I. water. Store in glass at room temperature for up to 1 year.

9.15. Wash Solution: Add 41 mL 6 N H_2SO_4 to about 500 mL D.I. water. Dissolve into this 50 g $NaH_2PO_4 \bullet H_2O$ and dilute to 1000 mL. Store at room temperature in glass for up to 1 year.

9.16. Hydrogen peroxide, H_2O_2, 30%. purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.17. Calibration Standards – For each standard concentration, add the volume of 1.0 mg/L working standard and the volume of DI listed below to the 1L separatory funnels and extract as a sample.

mLs Working Std. (1.0 mg/L)	mLs DI Water	Final (mg/L) Concentration
200	300	0.40
150	350	0.30
125	375	0.25
100	400	0.20
75	425	0.15
50	450	0.10
40	460	0.08
30	470	0.06
20	480	0.04
10	490	0.02
0	500	0.00

9.18. Low range Blank Spike (Low LCS): Add 0.1 mL working standard LAS solution (1.0 mg/L) to 500 ml DI. True Value = 0.02 mg/L Make fresh before use.

9.19. High range Blank Spike (High LCS): Add 2.0 mL working standard LAS solution (1.0 mg/L) to 499 mL DI. True Value = 0.40 mg/L. Make fresh before use.

9.20. CCV (0.30 mg/L): Add 150 mL Working Reference Solution (1.0 mg/L) to 350 mL DI. Make fresh before use.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11. PROCEDURE

11.1. Be sure the system has a current MDL and the analyst has a current Demonstration of Capability.

11.2. **Initial Calibration –**

11.2.1. The ICAL is extracted like the samples as described in the following sections.

11.2.2. The method of quantitation uses linear regression from the equation of a line ($y=mx+b$). The curve <u>must not</u> be forced through zero. The correlation coefficient must be ≥0.995. If this criteria is not met, outlier standards may be repeated for up to 24 hours and before the ICV is run.

11.2.3. The Initial Calibration curve may be used until QC samples indicate a need to recalibrate (see corrective actions for ICV, CCV, LL-LCS, HL-LCS).

11.2.4. ICV- The ICV is run immediately after the ICAL. The limit for the ICV is 80-120%. If this limit is not met, recalibrate.

11.3. Daily Calibration Verification

11.3.1. Each analytical day before samples are analyzed, the CCV must be analyzed to verify the ICAL. The CCV must be 80-120% of the true value. If it is not, correct the problem and repeat the CCV. If the CCV is still out, recalibrate. If it passes analysis may proceed.

11.3.2. The CCV must be analyzed every 10 samples and at the end of the run. If the CCV fails (outside 80-120% of the true value), a compliant CCV must be obtained before analysis can continue. Repeat any samples bound by the non-compliant CCV.

11.4. Prepare for Extraction

11.4.1. Apparatus Preparation: All glassware including glass wool should be rinsed with chloroform.

11.4.2. For unknown samples, select a sample volume consistent with the anticipated MBAS content. Shake the sample and estimate a dilution based on the persistence of bubble formation. Add 500 mL of sample or sample dilution to a 1 L separatory funnel.

11.4.3. Peroxide Treatment: If samples are suspected to contain sulfides, then samples, blanks, and standards alike should be pretreated with the addition of 1 mL 30% H_2O_2 and mixed thoroughly.

11.4.4. Solution Preparation: Add three drops of phenolphthalein indicator solution to each separatory funnel. Make each alkaline by dropwise addition of 1 N NaOH or until a stable dark pink color develops. Discharge pink color by dropwise addition of 1 N H_2SO_4 until pink color just disappears.

11.5. Ion pair formation

11.5.1. Add 25 mL methylene blue reagent and mix. Add about 20 mL $CHCl_3$ and rock vigorously for 1 minute (venting often). Let settle, swirl gently, and settle again. (Mix only one funnel at a time in order to vent often throughout the entire minute)

11.5.2. Draw off $CHCl_3$ layer into a 250 mL separatory funnel. Repeat extraction twice more adding 20 mL chloroform to the 1 L funnel each time.

Note: If blue color in water phase becomes faint or disappears, start over with a smaller sample aliquot adding D.I. water to a total volume of 500 mL. Excess methylene blue must be maintained.

11.6. Backwash of interferences

11.6.1. Add 50 mL of wash solution to the extracts in the 250 mL separatory funnel and shake vigorously for 1 minute. Let settle, swirl, settle, and draw off chloroform layer through a conditioned funnel and glass wool plug into a dried 100 mL volumetric flask. Extract wash solution twice with about 10 mL $CHCl_3$ each time and add these $CHCl_3$ extracts to the volumetric flask. Rinse wool and funnel into flask and make up to volume with chloroform and mix well.

11.7. **Spectrophotometric Measurement**:

11.7.1. Turn on the spectrophotometer and allow to warm for several minutes.

11.7.2. Adjust the spec to read at 652 nm.

11.7.3. Zero absorbance on the spec with the extracted blank.

11.7.4. Rinse the cell a couple of times with the extract to be measured. Clean the outside of the cell with a Kimwipe to remove dust and fingerprints.

11.7.5. Place the cell in the spec and place the cover over the cell holder.

11.7.6. Record absorbance on bench sheet.

11.8. Data Evaluation

11.8.1. Sample extracts which had a higher absorbance than the high standard must be reextraced using a dilution. Do not dilute the extract at the spec.

11.8.2. Check QC samples for acceptability. Repeat or flag samples as necessary.

12. QA/QC REQUIREMENTS

12.1. **ICV/CCV** – Frequency, limits, and corrective action are in the calibration sections in Section 11.

12.2. **Low Range LCS**:

12.2.1. Frequency -Performed at the rate of one for each batch of 1-20 investigative samples.

12.2.2. Limits - The result of the Low LCS must be within the limits set in the Wetchem QC Table in Appendix C of the Quality Assurance Manual.

12.2.3. Corrective Action - If it is not compliant, fix the problem and reextract the samples, volume permitting, or flag the associated data.

12.3. **High Range LCS**:

12.3.1. Frequency - Performed at the rate of one for each batch of 1 to 20 samples.

12.3.2. Limits - The result of the High LCS must be within 80-120% of the true value.

12.3.3. Corrective Action - If it is not compliant, fix the problem and reextract the samples, volume permitting, or flag the associated data.

12.4. DUP:

12.4.1. Frequency - Duplicate analyses are performed at the rate of one for each set of one to twenty samples. Do not choose field blanks for the analysis of a DUP.

12.4.2. Limits - If one or both of sample or duplicate is < 5X RL, the control limit is ± RL. The RPD value between sample results above 5X RL must meet the limits listed in Appendix C of the QAM

12.4.3. Corrective Action - If it is not compliant, , reanalyze the pair if deemed appropriate. The outlying RPD should be mentioned in the Case Narrative so that data may be flagged appropriately.

12.5. **Method Blank**:

12.5.1. Frequency - Performed at the rate of one for each batch of 1-20 samples.

12.5.2. Limits - The result of the MB must be below the reporting limit.

12.5.3. Corrective Action - If it is not compliant, fix the problem, obtain a compliant MB and reextact the samples, volume permitting, or flag the associated data.

13. DATA REDUCTION AND REPORTING

13.1. Results are reported as mg/L and calculated from the initial calibration curve using linear regression adjusted as follows:

$$\text{MBAS, mg/L} = \frac{\text{conc(mg/L) x 500 mL}}{\text{Sample volume (mLs)}}$$

13.2. Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

- Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

- Demonstration of Capability is performed upon instrument set-up , whenever a new analyst begins independent analysis, and annually thereafter according to ADM-TRANDOC and section 19 below. The documentation of this method performance is retained by the Quality Assurance office

- From Standard Methods 18th edition Method 5540C – *A synthetic sample containing 270 µg LAS/L in distilled water was analyzed in 110 laboratories with a relative standard deviation of 14.8% and a relative error of 10.6%. A tap water sample to which was added 480 µg LAS/L was analyzed in 110 laboratories with a relative standard deviation of 9.9% and a relative error of 1.3%. A river water sample with 2.94 mg LAS/L added was analyzed in 110 laboratories with a relative standard deviation of 9.1% and a relative error of 1.4%.*

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1. Chloroform waste is collected in the organic waste carboy to be disposed of by qualified personnel in the waste room. The aqueous layer is flushed down the drain.

15.2. It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when disposed of properly.

15.3. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

15.4. See SMO-SPLDIS for waste disposal practices and procedures.

16. CORRECTIVE ACTION FOR OUT OF CONTROL DATA

16.1. If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

17.1. If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, March 1983.

18.2. ASTM Method D2330-88

18.3. *Standard Methods for the Examination of Water and Wastewater*, 17th, 18th, and 20th Ed., Method 5540C.

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-

TRANDOC.

19.2. Observe Sample Preparation and Analysis. Follow Spectrophotometric Training Plan Form.

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Perform the analysis independently and show Initial Demonstration of Capability (IDC) by analyzing 4 replicates of a known mid-range standard in succession before client samples are analyzed. If recovery is within acceptable limits, complete IDC certificate and Training Plan Form and file with QA. Continuing Demonstration of Capability (CDC) will be demonstrated annually using a PE sample, single blind, or a new 4 replicate study.

20. METHOD MODIFICATIONS

20.1. None

21. INSTRUMENT-SPECIFIC ADDENDUM

21.1. None

22. ATTACHMENTS

Bench Sheet.

23. CHANGES FROM PREVIOUS REVISION

- Updated Benchsheet
- Added Sections 14, 16, 17, and 20 for NELAC compliance
- Modified wording in 1 for consistency with other SOPs. Eliminated MDL requirements from here.
- 1 – Eliminated sludges – this SOP does not cover adjustments for that matrix.
- 3.- Added Definitions of ICAL, QA/QC Samples, RPD, Batch, ICV, MDL, MRL
- 5 – Modified Safety section for consistency with other SOPs
- 6 - Added ASP holding time. Added that sample containers are purchased certified clean
- 8 - Added Maintenance Log section, spec to be calibrated every 6 months, reference to GEN-GC
- 9 - Changed the working stock and reference standard concentrations from 10 to 1 mg/L
- 9 - Changed the prep of the calibration standards, CCV, LCSs based on dilutions from 1 mg/L instead of 10 mg/L working stocks.
- 9 - Changed the expiration dates from “whichever is sooner” to “if no other indication is given”
- 11 - Modified format – added titles to sections
- 11 - Added need to check DOC and MDL

- 11 - Added recommendation not to dilute at the spec
- 11 - Added ICAL and Daily Cal sections
- 11 - Expanded upon Spec Measurement sections and data evaluation
- 12 - Added ICV/CCV and referenced 11
- 13 - Eliminated dilution in the calculation since final and initial volumes are included and there is not to be a dilution at the spec
- 14 - Modified for consistency with other SOPs.

Columbia Analytical Services
1 Mustard St., Rochester, NY

Surfactants (MBAS) by Method 425.1 **Curve Date:** ____________
MBAS, mg/L = Conc. (mg/L) x Dil'n x 500 ml / Sample amount **CC:** ____________

Analyst: ____________________ Date: __________ Time: ________ Pipet ID: _______

Sub. #	Order #	Sample Vol. (mLs)	Absorbance @ 652 nm	MBAS mg/L	Dilution Factor	Final Result mg/L
Standards:	0.00					
	0.02					
	0.04					
	0.06					
	0.08					
	0.10					
	0.15					
	0.20					
	0.25					
	0.30					
	0.40					
	ICV					
	ICB/PB					
	CCV					
	CCB/PB					
	LCS-LL					
	LCS-HL					

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STANDARD OPERATING PROCEDURE

AMMONIA by FLOW INJECTION ANALYSIS

SOP No.: GEN - 350.1
Revision 3

November 5, 2004

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: ______ Date: ___________
Initials: ______ Date: ___________
Initials: ______ Date: ___________

DOCUMENT CONTROL
NUMBER: ________________
Initials: ______ Date: ________

1. SCOPE AND APPLICATION

1.1. This SOP uses EPA method 350.1 to determine the concentration of Ammonia in drinking, ground, surface and saline waters, domestic and industrial wastes, and soils. The method is based on reactions that are specific for the ammonium (NH_4) ion.

1.2. The reporting limit is 0.05 mg/L for regular level water analysis and 0.01 mg/L for low level water analysis. The reporting limit is 5.00 mg/Kg for soils.

2. METHOD SUMMARY

2.1. This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

3. DEFINITIONS

3.1. **Initial Calibration** - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2. **QA/QC Samples** - Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.2.1. **Laboratory Control Sample (LCS)** - An artificial sample to which known quantities of the analyte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.2.2. **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of standard solutions of the analyte is added to a sample matrix prior to sample analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected.

3.2.3. **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.3. **Independent Calibration Verification (ICV) –** The ICV solution is made from a stock solution which is independent from the stock used to prepare calibration standards and is used to verify the validity of the calibration.

3.4. **Continuing Calibration Verification Standard (CCV) -** A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.5. **Instrument Blank (ICB/CCB) -** The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

3.6. **Relative Percent Difference (RPD) –** The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.7. Batch - Samples processed together as a unit, not to exceed 20 investigative samples. See ADM-BATCH for further discussion.

3.8. Method Detection Limit (MDL): a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.9. **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

4. INTERFERENCES

4.1. Calcium and magnesium ions may precipitate if present in sufficient concentration. EDTA or sodium tartrate is added to the sample in-line in order to prevent this problem.

4.2. Color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration through a 0.45µm filter. Sample color may be corrected for by running the samples through the manifold without color formation.

4.3. Samples with extreme pH will affect color development and result in a negative response. Samples and standards should contain approximately the same amount of chemical preservative.

4.4. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and any other sample processing apparatus that bias analyte response.

4.5. Contamination by carryover can occur when high level samples immediately precede samples containing significantly lower levels of contamination. Pay close attention to samples which follow high level samples. Re-analyze if contamination is suspected.

5. SAFETY

5.1. All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4. Refer to the Safety Manual for further discussion of general safety procedures and information.

5.5. The following chemicals have the potential to be highly toxic or hazardous. Consult specific MSDS.

- Sulfuric Acid (H_2SO_4)
- Sodium Nitroprusside ($Na_2Fe(CN)_5NO{\bullet}2H_2O$)
- Phenol, Liquefied (C_6H_5OH)

6. SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1. Samples should be collected in purchased, certified clean plastic or glass bottles or jars. Volumes collected should be sufficient to insure a representative sample, allow for replicate analysis (if necessary), and minimize waste disposal.

6.2. Water samples must be preserved with H_2SO_4 to a pH < 2. Water and soil samples are cooled to 0-6°C at the time of collection.

6.3. Samples are maintained at 0-6°C and must be analyzed within 28 days from collection.

6.4. For further sample handling, storage, and custody procedures, see SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. Balance - Analytical, capable of accurately weighing to the nearest 0.0001g.

7.2. Calibrated Micropipet, adjustable 100-1000µL or fixed at desired volume.

7.3. Calibrated repipetor (20.0 mL capacity).

7.4. Lachat QuikChem IV AutoAnalyzer or Lachat QC 8000 AutoAnalyzer. See Appendix A of the Quality Assurance Manual for computer hardware and software, configurations of specific components, serial numbers and receipt of major components.

7.5. Disposable beakers (dispo-cups)

8. PREVENTIVE MAINTENANCE

8.1. Nearly all of the components of the Lachat can be easily cleaned or replaced. The exception is the valve. When the valve becomes clogged it is necessary to have the unit sent out to be serviced. To avoid this expense and inconvenience, be sure sample cups, and dispo cups are free of particulates by rinsing thoroughly with D.I. water and drying. Visual inspection of this equipment is also recommended before analysis. Turbid samples should also be filtered to prevent valve clogs.

8.2. Be sure to change pump tubes regularly to ensure optimal performance.

8.3. Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

8.4. Prevent contamination - Keep the instrument and the bench area clean. Wipe down counters before and/or after use. Clean all glassware according to GEN-GC.

8.5. Troubleshooting – See instrument manual or maintenance log for help in solving specific analytical or instrument problems.

9. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1. Ammonium Chloride (NH_4Cl) – purchased commercially. Dry for two hours at 103-105°C. Cool to room temperature and store in a desiccator. Expires in 3 years.

9.2. **Standards Preparation General Information and Disclaimers**

All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 ppm standard may be made by adding 1 mL of 200 ppm to 10 mLs or may be made by adding 4 mL of 50 ppm to 10 mLs. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

The initial calibration curves given are typical, but also subject to variation due to detection levels needed. The lowest concentration level shall be at the method reporting level. The remaining levels should define the working linear range of the analytical system.

Vendors and vendors' products are sometimes listed for the ease of the analyst using this SOP, but products and purchased concentrations are examples only and subject to change at any time. All purchased standards are certified by the vendor. Certificates of Analysis are kept in the department until the standards are no longer being used – at which time they are filed with QA. Certificates of Analysis are available upon request. Purchased standards are routinely checked against an independent source for analyte concentration.

All Standards must be traceable using the CAS lot system (ADM-DATANTRY).

9.3. Nitrogen Calibration Standard Stock Solution (1000 mg N/L): In a 1-L volumetric flask, dissolve 3.819 g dried Ammonium Chloride (NH_4Cl) in about 800 mL reagent grade water (DI). Dilute to volume with DI water and invert several times until thoroughly mixed. Store at 0-6°C in amber glass. Discard after one year. **Note: This is the same standard as is prepared for total kjeldahl nitrogen analysis. The same stock may be used for both analyses.

9.4. Working Stock Solution (100.0 mg and 10.0 mg N/L): Dispense 9.00 mL of carrier into each of two dispo-cups using an adjustable repipettor or graduated pipet. Add 1.00 mL of 1000 mg/L standard stock solution to the first dispo-cup using an adjustable pipettor (This is 100.0 mg N/L). Mix and then transfer 1.00 mL of the 100 mg/L to the second dispo-cup and mix (This is 10.0 mg N/L). Prepare fresh each run.

9.5. Calibration Standards: Calibration standards are prepared directly into the carrier solution and analyzed. The EPA method requires at least 3 standards covering the range and a blank for calibration. Prepare standards in disposable beakers immediately prior to the analysis as follows:

Concentration (ppm)	Carrier (mL)	Working Stock 10 ppm (mL)
2.000	8.00	2.00
1.000	9.00	1.00
0.500	9.50	0.50
0.200	9.80	0.20
0.100	9.00	1.00 mL of 1.000 Std.
0.050	9.00	1.00 mL of 0.500 Std.
0.020	9.00	1.00 mL of 0.200 Std.
0.010	9.00	1.00 mL of 0.100 Std.
0.000	10.0	0.00

9.6. LCS / Matrix Spike (0.500 mg N/L): To 10.0 mL of carrier or sample, add 0.050 mL of 100.0 mg N/L working stock solution. Prepare fresh each run.

9.7. Nitrogen Calibration Reference Stock Solution (180 mg/L): In a 1-L volumetric flask dissolve 0.687 g dried Ammonium Chloride (NH_4Cl), second source, in about 800 mL reagent grade water (DI). Dilute to volume with DI water and invert several times until thoroughly mixed. Store at 0-6°C in amber glass for up to one year.

9.8. ICV/CCV (1.80 mg/L): Dispense 9.00 mL of carrier into each of two dispo-cups using an adjustable repipettor. Add 1.00 mL of reference stock solution to the first dispo-cup (This is 18.0 mg N/L). Mix and then transfer 1.00 mL of the 100 mg/L to the second dispo-cup and mix (This is 1.8 mg N/L). This is the working reference standard and will be used for the ICV and all CCV's. Prepare fresh each run.

9.9. Sulfuric Acid - (H_2SO_4) – Instra-Analyzed. Purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years if no other indication is given.

9.10. Carrier and Diluent: In a 1-L plastic bottle add 998 g Millipore DI water and 3.68 g Instra-Analyzed Sulfuric Acid. Invert several times until thoroughly mixed. Prepare fresh for each run.

9.11. Liquefied Phenol (C_6H_5OH) 88% - purchased commercially. Store in a flammable cabinet at room temperature. Expires upon manufacturer's indications, when color becomes darker than straw yellow or 3 years from receipt, if no other indication is given.

CAUTION: Phenol causes severe burns and is an extreme health hazard through skin absorption. Wear proper protective laboratory clothing including gloves and rinse any exposed skin IMMEDIATELY with copious amounts of water.

9.12. Sodium Hydroxide flakes (NaOH) – purchased commercially with special attention to ammonia content. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.13. Sodium Phenolate: To a tared 1 Liter amber glass jar add 888 g Millipore DI, 94.2 g of 88% liquefied Phenol (C_6H_5OH) and 32 g of Sodium Hydroxide flakes (NaOH). Stir until dissolved. Store at 0-6°C in an amber glass jar. Stable for one year. ***PREPARE IN HOOD!!***

9.14. Sodium Hypochlorite (6%): purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt if no other indication is given.

9.15. Sodium Hypochlorite working solution: In a 1L amber bottle add 300 mL 6% sodium hypochlorite and 300 mLs Millipore DI. Invert to mix. Prepare fresh for each run.

9.16. Disodium EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.17. Buffer Solution: In a 1-L glass amber jar, dissolve 50.0 g Disodium EDTA and 9.0 g NaOH in 965 g Millipore DI water. Stir until dissolved. Store in an amber glass jar at room temperature for up to one year.

9.18. Sodium Nitroprusside ($(Na_2Fe(CN)_5NO \cdot 2H_2O)$ – also called nitroferricyanide - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.19. Sodium Nitroprusside Color Reagent: In a 1-L amber glass jar dissolve 3.50 g Sodium Nitroprusside in 1000 g Millipore DI water. Stir until dissolved. Store in an amber glass jar at room temperature. Discard after one year.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11. PROCEDURE

11.1. Be sure the system has a current MDL and the analyst has a current Demonstration of Capability.

11.2. Sample Preparation

11.2.1. Soil samples – Weigh 1.0 g of sample into a clean, tared B-cup. Bring the total weight to 100 g with DI. Cap the cup and shake vigorously for 5 minutes.

11.2.2. Turbid water samples and prepared soil samples - filter through a syringe filter directly into the autosampler cup or into a dispo cup if dilutions are to be performed. If any samples are filtered, also filter a blank and an LCS. See GEN-FILTER for more information.

11.3. **Prepare standards and reagents** - as described in Section 9.

11.4. Instrument Setup

11.4.1. Adjust heating coil setting to 60°C. Turn on and allow to preheat.

11.4.2. Connect the manifold to the instrument (see attached manifold diagram). Inspect manifold for proper connections and appropriate sample loop (75cm) and wavelength filter (630nm) and heating coil length (650 cm). Place pump tubes loosely in their holders.

11.4.3. Once the heating coil has reached 60°C, place reagent feed lines in DI. Turn the pump on, adjust the tension of the pump tubes and inspect the system for leaks.

11.4.4. Load the method into the software and enter sample labels for the first tray in accordance with the analytical sequence described below. The method should be optimized from the suggested operating parameters listed in Section 17 using Graphical Events Programming. The Lachat software will calculate all dilutions provided the dilution information is entered.

11.5. Initial Calibration

11.5.1. The data system will prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation (see below). The ICAL must have at least 3 points which cover the calibration range and a blank. When more than 3 standards are analyzed, selected standards may be deleted to improve correlation coefficient to above 0.997 as long as the above ICAL requirements are met.

11.5.2. Calibration Curve, Linear Regression : This method of quantitation uses the equation of a line ($y=mx+b$). The curve <u>must not</u> be forced through zero.

11.6. **Analytical Sequence**:

Calibration Standards
ICV, ICB,LCS
10 samples
CCV,CCB
10 samples
CCV, CCB

Analyze CRDLs on the Lachat 8000 to see the response at the low end of the curve since the software does not convert the raw area counts of the standards into concentration in the calibration.

Continue with sequence until all samples are analyzed. The sequence must end with a CCV/CCB set. Insert DUP/MS where appropriate. Consult the QC section for further QC sample frequency requirements.

11.7 **Instrumental Analysis –**

11.7.1 Load the calibration standards and the samples into the autosampler as entered into the software with standards in order of decreasing concentration. Make sample dilutions with the diluent/carrier in compliance with ADM-DIL.

11.7.2 Place the feed lines in the appropriate reagents and allow to pump for about 5 minutes. *Note: Buffer Solution should be the first reagent introduced into the manifold and the color reagent should be the last reagent introduced into the manifold to prevent the formation of clogs due to reagent precipitate.

11.7.3 Run the standards, references, and samples. Be sure all ICAL and QC criteria is met and samples are within linear range. Repeat any samples at a dilution which are over the linear range (see ADM-DIL). Repeat any samples which may be influenced by carryover from the previous sample (response has not returned to baseline). Repeat any samples which have airpeaks which may influence the results. Repeat any samples which were incorrectly integrated by the software. Close with an acceptable CCV/CCB set.

11.7.4 When finished, place all lines in DI and rinse for about 5 minutes. Remove lines from DI and pump to dry for about 5 minutes. Turn off the pump and heating coil, and release tension on pump tubes.

11.7.5 Print the results and the calibration information immediately after the run. If any other runs are done before this information is printed, special care must be taken to ensure the correct calibration is applied to the results.

12. QA/QC REQUIREMENTS

12.1. An MDL study must be run annually. The result of the MDL must be less than the reporting limit. If it is not, correct the problem and repeat the study or raise the reporting limit. See ADM-MDL for more information.

12.2. Initial calibration requirements are given in the procedure (section 11)

12.3. ICV/CCV –

- Frequency - Analyze an ICV immediately after the initial calibration. Analyze a CCV after every 10 or fewer samples.
- Acceptance - Recovery must be 90-100% of the true value
- Corrective Action - Recalibrate if ICV fails. If a CCV fails, and acceptable CCV must be achieved before continuing. All samples bound by the unacceptable CCV must be reanalyzed.

12.4. ICB/CCB –

- Frequency -Analyze immediately after each ICV and CCV – every 10 samples.
- Acceptance - The result must be less than the reporting limit.
- Corrective Action - If the result is above the reporting limit, correct the problem and re-run the samples bound by the unacceptable CCB, or raise the reporting limit.

12.5. LCS –

- Frequency - Prepare one for every 20 samples.
- Acceptance - LCS recovery must be 90-110% of the true value.

- Corrective Action - If an LCS is out of control, correct the problem and reanalyze the affected samples or flag the data.

12.6. Duplicates –

- Frequency - Analyze one duplicate for every 10 or fewer samples. Do not choose field blanks as samples for the analysis of duplicates.
- Acceptance - The relative percent difference (RPD) between matrix duplicates should be 20 or less. If one or both of sample or duplicate is < 5X RL, the control limit is ± RL.
- Corrective Action - If they are not, repeat the original and the duplicate or flag the affected data.

12.7. Matrix Spike –

- Frequency - Analyze one matrix spike for every 10 or fewer samples. Do not choose field blanks as samples for the analysis of the MS.
- Acceptance - Matrix spike recovery must be within the limits in the Wetchem QC table in the Quality Assurance Manual.
- Corrective action - if recovery of the MS fails on a sample, the batch is considered acceptable as long as the LCS meets acceptance criteria. It is recommended that the MS/MSD be reprepared and reanalyzed to confirm the outliers, however it is not required due to probable matrix interferences. Flag the outlier.

13. DATA REDUCTION AND REPORTING

13.1. Calculations: Lachat software will calculate all results from the regression equation, including those with dilution's, provided that the correct dilution information was entered. Soil samples are entered with a 100 fold dilution in the Lachat software to account for the 1g to 100 mL extraction, but the dilution is entered as straight in the LIMS since this is the lowest possible dilution. The MRL in LIMs is based on this assumption.

13.2. Report results to 3 significant figures. Water samples are reported in mg N/L. Soil samples are reported in mg N/Kg.

13.3. Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

Demonstration of Capability is performed upon instrument set-up , whenever a new analyst begins independent analysis, and annually thereafter according to ADM-TRANDOC and section

19 below. The documentation of this method performance is retained by the Quality Assurance office.

"In a single laboratory (EMSL-Cincinnati), using surface water samples at concentrations of 1.41, 0.77, 0.59, and 0.43 mg NH3-N/L, the standard deviation was ±0.005.

In a single laboratory (EMSL-Cincinnati), using surface water samples at concentrations of 0.16 and 1.44 mg NH3-N/L, recoveries were 107% and 99%, respectively.

Interlaboratory precision and accuracy data in Table 1 were developed using a reagent water matrix. Values are in mg NH3-N/L."

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

15.1. It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

15.2. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual. Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

15.3. All used reagent is collected in a container and disposed of into an inorganic waste carboy for proper disposal.

15.4. Samples are disposed according to SMO-SPLDIS.

16. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. *Methods for Chemical Analyses of Water and Wastewater*, USEPA, EPA-600/4-79-020, March 1983. Method 350.1

18.2. *Methods for the Determination of Inorganic Substances in Environmental Samples*, USEPA, EPA/600/R-93/100 August 1993. Method 350.1

18.3. Lachat QuikChem Method [10-107-06-1-B].

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2. Observe Sample Preparation and Analysis. Follow Lachat Training Plan Form (May be found on the Rochester CASLAB Intranet at P:\INTRANET\QAQC\TRAINING\QAforms.HTM.)

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Observe Instrument Operation and Maintenance.

19.5. Perform an IDC (Initial Demonstration of Competency) by independently analyzing four mid-range standards prior to analyzing client samples. If recovery is within acceptable limits, complete Training Plan Form and file with QA. Continuing proficiency (CDC) will be demonstrated annually using a PE, a single blind, or a new 4 replicate study.

20. METHOD MODIFICATIONS

- The samples are not distilled but are heated during the automated colorimetry.
- The samples are not pH adjusted but the carrier and the buffer compensate.

21. INSTRUMENT-SPECIFIC ADDENDUM

The Lachat Suggested Operating Parameters for the Quikchem 8000

Pump Speed:	35
Cycle Period:	60

Analyte Data:

Concentration Units:	mg N/L
Peak Base Width:	27.0 s
% Width Tolerance:	100
Threshold:	10000
Inject to Peak Start:	41.8s
Chemistry:	direct

Calibration Data:

Calibration Fit Type: 1st Order Polynomial
Calibration Rep. Handling: Average
Weighting Method: None
Concentration Scaling: None
Force through Zero: No

Sampler Timing:

Min. Probe in Wash Period: 5.0s
Probe in Sample Period: 24s

Valve Timing:

Load Time: 0.0s
Load Period: 15s
Inject Period: 45s

22. ATTACHMENTS

- Manifold Diagram.
- Calibration Standard Preparation - for use at the bench.
- Table 1 – Interlaboratory precision and Accuracy Data.

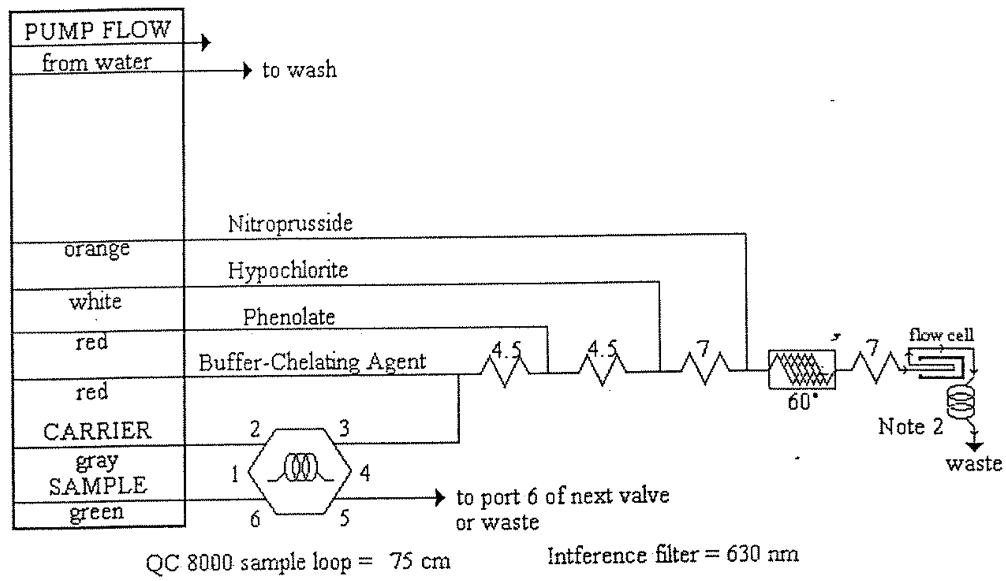
23. CHANGES FROM PREVIOUS REVISION

- Added reporting limit for soils in 1
- Added Definitions for MRL, MDL, Batch, RPD, Initial calibration in 3
- Updated safety in 5 for consistency
- Added soils to 6 for preservation
- Referenced Appendix A for instrument configuration in 7.4
- Updated Maintenance Log in 8 for consistency
- Referenced GEN-GC in 8
- Added Troubleshooting in 8
- Added Standards Prep General Info and Disclaimers in 9
- 9 - Changed need for 5 standards to 3 standards and a blank as required by method.
- Changed reference of :whichever is sooner" to "if no other indication is given" for expiration of reagents.
- Added need to check for current MDL and DOC in 11
- Added headings in 11 to break it up – Sample prep, Instrument Setup, ICAL, Instrumental Analysis
- Added sample prep for soils – expanded upon filtering of water samples
- Expanded upon what samples needed to be repeated in 11
- Added need to print calibration and analysis data immediately after analysis in 11
- Broke out the frequency, acceptance criteria, and corrective action in 12 for each QC item
- Added control limit for low level dups in 12
- Added that field blanks are not to be chosen for matrix QC

- Removed ICAL acceptance from 12 and referenced 11
- Expanded upon the calculation of soils in 13 and added soil units
- Removed statement regarding dilutions in 13 – included in 11
- Expanded upon method performance in 14 – included text and table from method
- Updated 15 for consistency
- Added reference to Training Plan Form on Intranet in 19.
- Added attachments for Calibration standards and method performance

TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

AMMONIA MANIFOLD DIAGRAM



CARRIER is Reagent 5.

Manifold tubing is **0.8 mm (0.032 in) i.d**. This is **5.2 uL/cm.**

4.5	is	**70**	cm of tubing on a 4.5 cm coil support
7	is	**135**	cm of tubing on a 7 cm coil support

APPARATUS: The [heater symbol] indicates 650 cm of tubing wrapped around the heater block at the specified temperature.

Note 1: TYGON PUMP TUBES MUST BE USED FOR THIS METHOD

Note 2: 200 cm x 0.022" i.d. backpressure loop.

AMMONIA (2.000 - 0.000 (pql=0.010mg/L))

A.) 10.0 ppm WORKING STOCK:
do two (2) 1/10 serial dilutions of the 1000 ppm NH_3 / TKN Standard Stock. Prepare these dilutions with Carrier-Diluent, as well as all standards, references, and sample dilutions.

B.) STANDARDS:

conc. (mg/l)	mls 10.0 ppm	mls Carrier-Diluent
a.) 2.000	2.00	8.00
b.) 1.000	1.00	9.00
c.) 0.500	0.50	9.50
d.) 0.200	0.20	9.80
e.) 0.100	1/10 dil'n of b.) 1.000	
f.) 0.050	1/10 dil'n of c.) 0.500	
g.) 0.020	1/10 dil'n of d.) 0.200	
h.) 0.010	1/10 dil'n of e.) 0.100	
i.) 0.000	10 mLs of Carrier-Diluent	

C.) ICV / CCV: (True Value = 1.80 mg/l)
do two (2) 1/10 serial dilutions of 180 ppm NH_3 Reference Stock Solution. Make with Carrier-Diluent.

D.) LCS / Matrix Spike: (True Value = 0.500 mg/l)
10.0 mls Carrier-Diluent / sample + 0.050mls 100 ppm Working Stock.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. INTERLABORATORY PRECISION AND ACCURACY DATA

NUMBER OF VALUES REPORTED	TRUE VALUE (T)	MEAN (X)	RESIDUAL FOR X	STANDARD DEVIATION (S)	RESIDUAL FOR S
134	0.270	0.2670	-0.0011	0.0342	0.0015
157	0.692	0.6972	0.0059	0.0476	-0.0070
136	1.20	1.2008	0.0001	0.0698	-0.0112
195	1.60	1.6095	0.0076	0.1023	0.0006
142	3.00	3.0128	0.0069	0.1677	-0.0067
159	3.50	3.4991	-0.0083	0.2168	0.0165
156	3.60	3.5955	-0.0122	0.1821	-0.0234
200	4.20	4.2271	0.0177	0.2855	0.0488
196	8.76	8.7257	-0.0568	0.4606	-0.0127
156	11.0	11.0747	0.0457	0.5401	-0.0495
142	13.0	12.9883	-0.0465	0.6961	0.0027
199	18.0	17.9727	-0.0765	1.1635	0.2106

REGRESSIONS: X = 1.003T - 0.003, S = 0.052T + 0.019

STANDARD OPERATING PROCEDURE

TITRAMETRIC DETERMINATION OF TOTAL ALKALINITY

GEN-310.1

Revision 3

March 28, 2002

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: ______ Date: ___________
Initials: ______ Date: ___________
Initials: ______ Date: ___________

DOCUMENT CONTROL

NUMBER: _______________

Initials: ______ Date: ______

1. SCOPE AND APPLICATION

This method (EPA 310.1) is applicable to the measurement of alkalinity in drinking, surface, and saline waters, domestic and industrial wastes for all concentration ranges. The Reporting limit is 2.0 mg/L.

2. METHOD SUMMARY

An unaltered sample is titrated to an endpoint of a pH of 4.5 using a pH meter. The procedure determines a sample's acid-neutralizing capacity, which is the sum of its titratable bases.

3. DEFINITIONS

3.1. **Initial and Continuing Calibration Verification (ICV/CCV) –** The ICV/CCV solution is used to verify the validity of the meter calibration and performance of the test.

3.2. **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of solution of the analyte is added to a sample matrix prior to sample analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected.

3.3. **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4. **Instrument Blank (ICB/CCB) -** The blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (DI in this test). The purpose of the CCB is to determine the levels of contamination associated with the analysis.

3.5. **Laboratory Control Standard (LCS) -** In the LCS or blank spike analysis, predetermined quantities of solutions of the analyte are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected and used to verify the validity of the test.

3.6. **Batch –** Unit of samples run together on the same day, not to exceed 20 samples.

4. INTERFERENCES

4.1. High sodium concentration at pH > 10 can cause error.

4.2. Samples containing oil may coat the electrode and cause a sluggish response or inaccurate readings. Rinse the probe with methanol after analysis of an oily sample before running other samples.

4.3. Suspended matter or precipitates formed during the titration may cause a sluggish electrode response.

5. SAFETY

5.1. Wear gloves, lab coat, and safety glasses when handling samples and reagents.

6. SAMPLE COLLECTION, CONTAINERS, AND STORAGE

Samples are to be collected with no headspace in plastic bottles with no chemical preservative. Cool to 0-6 ° C until analysis. Routine Holding time is 14 days. Holding time for ASP work is 12 days from VTSR (Verified Time of Sample Receipt). Sample handling, storage, and custody procedures are discussed in SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. pH meter with electrode which reads to 0.01 pH units and temperature compensation probe. The two probes currently in use are an Orion glass bulb probe and the digital Intelli Probe.

7.2. Titration buret apparatus.

7.3. Magnetic stirrer, pipets, beakers and stir bars.

8. PREVENTIVE MAINTENANCE

8.1. Store Orion glass bulb pH probe in solution of 0.5 g KCl and 100 mL pH 7 buffer.
Store Intelli Probe in plastic sleeve with a drop of water (do not submerge)

8.2. Change filling solution in the Orion glass bulb probe weekly.
Use a toothbrush and mild soap solution to clean the electrode on the Intelli Probe.

8.3. Place parafilm or a cap on the top of the buret when not in use to prevent contamination of titrant.

9. REAGENTS AND REFERENCE SOLUTIONS

9.1. Sulfuric Acid (0.0200 N): Certified, purchased commercially. Store at room temperature. Expires upon manufacturer's indications or one year from receipt, whichever is first. Standardization is not required if the solution is purchased commercially and there is no more than a single dilution made during preparation. Store at room temperature. If the 0.02 N acid is not purchased as stated above, standardization shall be required. See Method 310.1 Section 5.

9.2. Reference Stock Standard (5000 mg/L $CaCO_3$): Dissolve 5.300 g Na_2CO_3 in DI water and dilute to 1 liter volumetrically. Store refrigerated at 0-6°C in a plastic container for up to 6 months.

9.2.1. High Level ICV and CCV: Titrate 2.0 ml of 5000 mg/L Reference Stock. True Value = 5000 mg/L

9.2.2. High Level LCS: Dilute 5.0 mL 5000 mg/L Reference Stock to 25 mL DI water. True value = 1000 mg/L

9.2.3. High Level Matrix Spike: To the MS sample aliquot, add a volume of 5000 mg/L Reference stock equivalent to at least ¼ of the value of the sample.

9.3. Spike Stock Solution (1000 mg/L $CaCO_3$): Dissolve 1.0589g Na_2CO_3 in DI water and dilute to 1.0 liter volumetrically. Store refrigerated at 0-6°C in a plastic container for up to 6 months.

9.3.1. Low/Regular Level LCS: Add 2.0 mL 1000 mg/L Spike Stock Solution to 100 mL DI water. True value = 20 mg/L

9.3.2. Regular level Matrix Spike: To the MS sample aliquot, add a volume of 1000 mg/L spike solution equivalent to at least ¼ of the value of the sample.

9.4. Reference Solution (50 mg/L as $CaCO_3$) Volumetrically dilute 10.0 ml of 5000 mg/L Stock Solution to 1.0 liter with DI water. Store refrigerated at 0-6°C in a plastic container for up to 6 months.

9.4.1. Low/Regular Level ICV and CCV: Titrate 25 ml of the 50 mg/L Reference Solution. True Value = 50 mg/L

9.5. Blank (ICB/CCB)- titrate 100 mLs DI.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11. PROCEDURE

11.1. Calibrate the pH meter according to manufacturer's instructions using buffers 4 and 10 and checking the calibration with the pH 7 buffer. Record all pertinent meter calibration information in the pH meter book and in the spreadsheet.

11.2. Remove parafilm or cap from buret. Rinse and zero the buret with the appropriate titrant. Low level and regular level samples use the same titrant and may be run with the same QC. High level samples require a separate titrant and require a run separate from the low and regular samples. The high level run will require its own QC.

11.3. Place up to 100 mLs of sample, a small stirbar and the probes into a beaker. It is recommended to start with 10-25 mLs sample for most clients. See the Reagents section for the appropriate volumes for the ICV, ICB, LCS. Be sure the sample covers the glass bulb of the probe (if applicable). Place the beaker under the tip of the buret in such a way that the titrant will drip directly into the sample without first hitting the probes or the side of the beaker.

11.4. Record the ID of the pipet used to spike LCSs and MSs.

11.5. Record the initial pH of the sample.

11.6. Record the initial reading of the buret.

11.7. Add titrant until the meter reads 4.5, being careful to add titrant dropwise as the endpoint is neared. The endpoint is the drop of titrant which drops the pH to or below 4.5. Record the final reading of the buret.

11.7.1. If the sample used less than 2 mLs of titrant, repeat the test with more sample (up to 100 mLs) or add a measured volume of sample and continue titrating in order to obtain good precision. Record the total sample volume on the spreadsheet.

11.7.2. If the sample requires a large amount of titrant (more than 25 mLs) repeat the test with less sample in order to obtain a sharp endpoint.

11.7.3. HIGH LEVEL - If when using the 0.02 N titrant, more titrant is used than samples was used, the value will be greater than 1000 mg/L and the test should be repeated using the high level titrant (0.100N).

11.7.4. LOW LEVEL - If the sample concentration is less than 20 mg/L, record the titrant volume and exact pH at the endpoint and continue titrating to an additional 0.3 pH units lower.

11.7.5. CARBONATE OR BICARBONATE - If the carbonate, bicarbonate, or hydroxide alkalinity is requested and the initial pH is greater than 8.3, record the volume of acid used to lower the pH to 8.3. Use this volume to calculate the PHENOLPHTHALEIN ALKALINITY. Continue to titrate to pH 4.5 and record the titrant volume to obtain the total alkalinity. Refer to the table in the calculation section to calculate the carbonate and bicarbonate alkalinity.

11.8. The Analytical Sequence should follow the following order:

ICV
Blank
LCS

Up to 9 more samples including a DUP and MS

CCV
CCB

Up to 10 samples including a DUP and MS.

CCV
CCB
LCS

Etc., closing with a CCV/CCB

11.9. When finished with the test, replace cap or parafilm on buret. Cover the filling hole in the Orion glass bulb probe and place it in its storage solution. Clean the electrode of the Intelli Probe with a toothbrush and soap and place it in its plastic sleeve with a drop of water (do not submerge).

12. QA/QC REQUIREMENTS

12.1. Run an ICV before any other samples. The result of the ICV shall be within the limits set forth in the Wetchem QC table in the Quality Assurance Manual. If it is not, determine the cause of the problem and obtain a compliant ICV before running any samples.

12.2. Run an ICB immediately after the satisfactory ICV. The result of the ICB shall be less than the PQL. If it is not, determine the cause of the problem and obtain a compliant ICV/ICB set before continuing.

12.3. Run a CCV/CCB set after every 10 samples and at the close of the day's run. The results shall follow the limits stated for the ICV and ICB. If they do not, determine the cause of the problem, obtain a compliant CCV/CCB set and repeat any samples bound by the out of control CCV/CCB set.

12.4. Run duplicates at a 10% frequency. The DUP should have a RPD as set forth in the Wetchem QC table or +/- PQL if results are less than 5X the PQL. If noncompliant, repeat the sample and duplicate or flag the associated sample results in the batch.

12.5. Run matrix spikes at a 10% frequency. The MS should have a % recovery within the limits set forth in the Wetchem QC table. If it does not, repeat the MS to confirm the failure or flag the associated sample results in the batch.

12.6. Run an LCS per batch of 20 samples. The LCS recovery should be within the limits set forth in the Wetchem QC table. If it is not, determine the cause, fix the problem, obtain a compliant LCS, and repeat any associated samples.

13. DATA REDUCTION AND REPORTING

13.1. **CALCULATIONS**:

13.1.1. Low Level:

$$Alkalinity,\ mg\ /\ L\ \ CaCO_3 \ = \ \frac{(2B\ -\ C)\ x\ N\ x\ 50{,}000}{ml\ Sample}$$

Where: B=ml titrant used to pH 4.5
C=Total ml titrant used to pH exactly 0.3 less than actual 4.5 endpoint
N=Normality of titrant used

13.1.2. Regular and High Level:

$$Alkalinity,\ mg\ /\ L\ \ CaCO_3 \ = \ \frac{A\ x\ N\ x\ 50{,}000}{ml\ Sample}$$

Where: A=ml titrant used to pH 4.5
N=Normality of titrant used

13.1.3. Calculate Hydroxide, Carbonate, and/or Bicarbonate alkalinity as mg/L $CaCO_3$ according to the following table.

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P=0	0	0	T
P<1/2T	0	2P	T-2P
P=1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P=T	T	0	0

P = Phenolphthalein Alkalinity
T = Total Alkalinity

13.2. **REPORTING AND DOCUMENTATION**

13.2.1. Record all numbers on spreadsheets to three significant figures and report alkalinity as mg/L $CaCO_3$.

13.2.2. PQL (Practical Quantitation Limit) = 2 mg/L $CaCO_3$.

13.2.3. Data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

Samples and titrated samples may be washed down the drain. See SMO-SPLDIS for further discussion on waste management.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. Method 310.1, *Methods for Chemical Analysis of Water and Wastes*, EPA- 600/4-79-020, Revised March 1983.

18.2. Method 2320 B in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2. Observe Sample Preparation and Analysis. Follow Training Plan Form.

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Demonstrate Competency by performing the analysis independently. Analyze 4 replicates of a known proficiency or standard. If recovery is within acceptable limits, complete Training Plan Form, summary spreadsheet, IDC certificate and file with QA. Continued proficiency shall be demonstrated using outside PE source, an LCS, an internal unknown, or a new 4 replicate study.

20. METHOD MODIFICATIONS

None

21. INSTRUMENT ADDENDUM

None.

22. ATTACHMENTS

Spreadsheet

23. CHANGES FROM PREVIOUS REVISION

- Added sections 14, 16, 17, and 20 for NELAP compliance.
- Added the Intelli Probe and its storage and maintenance in 7, 8.1, 8.2, 11.3, 11.9
- Changed the wording in 11.2 for clarity.
- Added ASP holding time to section 6.
- Changed references of benchsheet to spreadsheet.

Columbia Analytical Services
1 Mustard Street
Rochester, NY 14609

Alkalinity: Regular / High Level
Method: 310.1

Analyst: ____________
Date: ____________
Time: ____________
Pipette: ____________

pH meter cal: Buffer Lot #:
4.0 ________ ________
7.0 ________ ________
10.0 ________ ________

Phenolphthalein alkalinity = the quantity measured by titration to pH 8.3

$$\text{Alkalinity, mg } CaCO_3\text{/L} = \frac{A \times N \times 50{,}000}{\text{mL sample}}$$

where: A = mL standard acid used
N = normality of H_2SO_4 = 0.1000

Date H_2SO_4 was received: ____________
Reference#: ____________

Table 403.1 Alkalinaty Relationships

Result of titration	Hydroxide Alkalinaty as $CaCO_3$	Carbonate Alkalinaty as $CaCO_3$	Bicarbonate oncentration as $CaCO_3$
P = 0	0	0	T
P < 1/2T	0	2P	T - 2P
P = 1/2T	0	2P	0
P > 1/2T	2P - T	2(T- P)	0
P = T	T	0	0

P = Phenolphthalein Alkalinaty T = Total Alkalinaty

	Job #	Order #	Smpl. Vol.	pH Init.	Titr. Vol. Init.	Vol. @pH 4.5	Vol. @pH 8.3	Phen. Alk.	OH- Alk.	Carb. Alk.	Bicarb. Alk.	Total Alk.
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												
16												
17												
18												
19												
20												
21												
22												
23												

ALKALINITY LOW

Columbia Analytical Services
1 Mustard Street
Rochester, NY 14609

Alkalinity: Low Level (<20 MG/L)
Method: 310.1

Analyst: ____________
Date: ____________
Time: ____________
Pipette: ____________

pH meter cal: Buffer Lot #:

4.0 ________   ________
7.0 ________   ________
10.0 ________   ________

$$\text{Alkalinity, mg } CaCO_3 \text{ /L} = \frac{(2B-C) \times N \times 50{,}000}{\text{mL sample}}$$

where: B = mL standard acid used
C = **total ml titrant to reach 0.3 pH units lower**
N = normality of H_2SO_4 = 0.0200

Date H_2SO_4 was received: ____________
Reference#: ____________

	Job #	Order #	Smpl. Vol.	pH Init.	Titr. Vol. Init.	Vol.@pH 4.5		Vol.@pH -0.3		Total Alk.
						Vol.(B	pH	Vol.(C)	pH	
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										

STANDARD OPERATING PROCEDURE

TOTAL ORGANIC CARBON IN WATER

GEN-415.1/9060

Revision 5
August 16, 2004

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed
and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: __________

1. SCOPE AND APPLICATION

1.1. This procedure is applicable to the determination of Total Organic Carbon (TOC) in drinking and surface waters, domestic and industrial wastewater using methods 415.1 and 9060. The procedure may also be extended to certain domestic or industrial wastes.

1.2. Normal operating parameters (i.e. 1 ml sample loop) yield a Reporting Limit of 1.0 ppm C. A 10 ml sample loop may be used to lower the reporting limit to 0.05 ppm C.

2. METHOD SUMMARY

2.1. Total Organic Carbon (TOC) is determined by measuring carbon dioxide released by chemical oxidation of the non-purgeable organic carbon in the sample. After the sample has been acidified and purged of inorganic carbon, sodium persulfate, a strong oxidizer, is added. This oxidant quickly reacts with non-purgeable organic carbon in the sample at 100°C to form carbon dioxide. When the reaction is complete, the carbon dioxide is purged from the solution, concentrated by trapping, and thermally desorbed (200°C) and carried into a non-dispersive infrared detector that has been calibrated to directly display the mass of carbon dioxide detected. The resulting carbon mass in the form of carbon dioxide is the equivalent to the mass of organic carbon originally in the sample.

3. DEFINITIONS

3.1. **High Level** = using the 1.0 mL sample loop which creates a working range of 1.0 to 30.0 ppm.

3.2. **Low Level** = using the 10.0 mL sample loop which creates a working range of 0.05 to 1.00 ppm.

3.3. **Independent Calibration Verification (ICV) –** The ICV solution is made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.4. **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis

3.4.1. **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of standard solution is added to a sample matrix prior to sample analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected.

3.4.2. **Duplicate Sample (DUP)** - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4.3. **Laboratory Control Standard (LCS)** - In the LCS or blank spike analysis, a predetermined quantity of standard solution is added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected and used to verify the linear range daily.

3.5. **Continuing Calibration Verification Standard (CCV)** - A reference analyzed daily at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.6. **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (DI in this test). The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

3.7. **Relative Percent Difference (RPD) –** The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.8. **Batch –** Unit of samples prepared together on the same day, not to exceed 20 field samples. See ADM-BATCH for further discussion of batches.

3.9. **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.10. **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

3.11. **Initial Calibration -** analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

4. INTERFERENCES

4.1. Positive bias may be caused by contaminants in the gas, dilution water, reagents, glassware, or other sample processing hardware. The use of high purity reagents and gases help minimize interference problems. An average reagent blank value is determined by analyzing the reagents and is used by the Model 1010 for correction in calculation of TOC.

4.2. Interference by non-CO_2 gases: The infrared detector is sensitized to carbon dioxide and accomplishes virtually complete rejection of response from other gases which absorb energy in the infrared region. Trapping and desorption of carbon dioxide on the molecular sieve trap isolates the component of interest and allows the complete absence of interference in the system from gases other than carbon dioxide.

4.3. Contamination by carryover can occur when high level samples immediately precede samples containing significantly lower levels of contamination. Pay close attention to samples which follow high level samples. Re-analyze if contamination is suspected.

4.4. Interference by chloride:

4.4.1. High levels of chloride ion present analytical problems not adequately addressed by EPA 415.1/9060. The major interferences associated with the analysis of seawater are overcome by maintaining effective Sample: Oxidant ratios, and allowing sufficient analysis time.

4.4.2. Chloride ions compete directly with carbon for available persulfate ions. In seawater and brine, the amount of chloride present in a sample is much greater than the organic carbon present. In these cases the recovery of TOC will suffer due to incomplete oxidation. Some precautions that can be taken are to increase reaction time and increase the volume and concentration (250g/L) of the persulfate reagent used during analysis. An increase in persulfate to 4000 uL/sample will provide enough persulfate so that the organic carbon is able to oxidize.

4.4.3. The oxidation process of organic compounds by persulfate generally follows first order reaction kinetics. The oxidation of chloride to chlorine introduces intermediate steps, which result in a more complex reaction. This reaction proceeds more slowly. By extending the reaction time to 5 minutes, the reaction will have time to finish, resulting in complete oxidation of all the organic carbon present in the sample.

4.5. Consult Model 1010 users' manual pages 51-54 for more information pertaining to difficult sample matrices.

5. SAFETY

5.1. All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Sodium Persulfate is a strong oxidizer and should be handled with extreme care.

5.4. Phosphoric Acid is a corrosive material should be handled with extreme care.

5.5. Potassium Biphthalate is a chemical irritant and may cause eye burns.

5.6. The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

5.7. Refer to the Safety Manual for further discussion of general safety procedures and information.

6. SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1. For most accurate analyses, sampling containers should be free of organic contaminants.

6.2. Sampling and storage of samples in glass bottles is preferable. If this is not feasible, sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. This lab uses purchased, certified clean 40 mL glass vials with Teflon septa caps in its bottle sets.

6.3. Because of the possibility of oxidation or bacterial decomposition of certain components, the samples should be kept cool (0-6°C) and protected from sunlight and atmospheric oxygen. The sample must be acidified ($pH < 2$) with HCL or H_2SO_4. This lab uses H_2SO_4. Once preserved, samples must be analyzed within 28 days from collection. For ASP work, samples must be analyzed within 26 days from VTSR (Verified Time of Sample Receipt).

6.4. Sample handling, storage, and custody procedures are discussed in SOP SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. Model 1010 Total Organic Carbon Analyzer: Utilizes classic persulfate oxidation method. (O.I. Analytical)

7.2. Autosampler: OI Analytical Model 1051 Vial Autosampler

7.3. Glassware:

7.3.1. Class A volumetric pipettes of assorted volumes

7.3.2. Class A volumetric flasks of assorted volumes

7.4. Printer

7.5. Computer with OI Analytical's "WinTOC" software for control of the Model 1010 TOC Analyzer

8. PREVENTIVE MAINTENANCE

8.1. For the most reliable performance of the instrument, the following schedule of routine maintenance is suggested but not mandatory:

8.1.1. Daily and/or Weekly, as necessary:

8.1.1.1. Check gas cylinder supply. Replace as necessary.

8.1.1.2. On Mondays: refill the reagent reservoirs and then run the "Monday Blanks" sequence. This sequence will run 2 sets of 10 reagent blanks and 4 sets of quadruplicate blanks.

8.1.1.3. Check DI water flask, be sure it is full and being purged. Empty the flask and rinse with 50/50 HCL then DI then Ultra Pure DI if algal growth appears.

8.1.1.4. **Instrument, Diagnostics**: Calibrate the Autosampler: Click "Home", wait for tray to move to home, then click "Go To First Vial", then click "Calibrate". The software will prompt user to place the first vial beneath the needle port, then click "OK". Double check calibration by clicking "Needle Down", check that the needle is centered in the vial, then click "Needle Up". Click "OK" to get out of this menu.

8.1.2. Quarterly and/or before new calibration curves:

8.1.2.1. Zero the NDIR cell (page 59, ops manual)
8.1.2.2. Check flares and connections
8.1.2.3. Rinse the system with persulfate: place "Rinse In" line into "Sample In" port. Place the end of the "Rinse In" line into the persulfate reagent. Run a schedule of 3 or 4 blanks, with the

sample volume set to 20 mL. Replace the lines back to normal, and run numerous DI blanks until the system has stabilized.

8.1.3. Semi-annually and/or before new calibration curves:

8.1.3.1. Sample pump: check and if necessary, replace the peristaltic pump tubing (page 59, ops manual).

8.1.3.2. Digestion vessel and Condensation Chamber: check and clean if necessary (page 60, ops manual)

8.1.3.3. Replace or clean the permeation tube (page 62, ops manual)

8.1.4. On an As-needed basis:

8.1.4.1. Leak check the system, whenever the instrument suddenly does not operate as consistently as previously: Instrument menu, Diagnostics, Leak Check (page 64, ops manual, see also "Flow Adjustment", page 66 ops manual)

8.1.4.2. Indicating Drying Tube: replace or refurbish if the desiccant inside has changed color from blue to pink, or if a leak is found around one of the end fitting of the tube (page 58, ops manual)

8.1.4.3. NDIR Linearization check: see page 62-63, ops manual

8.1.4.4. See Chapter 7 of ops manual for further Troubleshooting information.

8.2. Maintenance Log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The data file name of the first acceptable run after maintenance is to be documented in the maintenance log.

9. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1. Ultra Pure DI - Reagent (laboratory deionized) water that has passed through the Millipore system in the Volatiles laboratory.

9.2. Sodium Persulfate ($Na_2S_2O_8$)– purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.3. 10% Sodium Persulfate:

Prepare solution of sodium persulfate by dissolving 100 g $Na_2S_20_8$ into Ultra Pure DI water in a 1 liter volumetric flask. For seawater analyses prepare a 250 g/L solution by dissolving 250 g of sodium persulfate into DI in a 1 Liter volumetric flask. Store in amber glass at room temperature for up to 1 year.

9.4. Phosphoric Acid – 85% - ACS reagent grade - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.5. Phosphoric Acid (5%):

Prepare 5% by volume solution of phosphoric acid by adding 59 mL of 85% H_3PO_4 to reagent water (1 liter total volume). Store in amber glass at room temperature for up to 1 year.

Note: If high organic contamination of acid solution is suspected, see Model 1010 user manual (pg. 12) for steps necessary to purify solution.

9.6. ICV/CCV:

The ICV and CCV is prepared by diluting 4.0 mLs of 1000 ppm KHP reference stock solution to 200 mLs with Ultra Pure DI in a class A volumetric flask. Resulting concentration is 20.0 ppm. For low level analysis, dilute 0.15 mLs of the 1000 ppm KHP reference stock solution to 200 mLs with Ultra Pure DI in a class A volumetric flask, TV = 0.75 mg/L. Prepare fresh daily or as needed.

9.7. Laboratory Control Sample (LCS):

The LCS is prepared by diluting 1.00 mL of 1000 ppm KHP standard stock solution to 100 mLs with Ultra Pure DI in a class A volumetric flask. The resulting concentration is 10.0 mg/L. For low level analysis, dilute 0.025 mL of 1000 ppm KHP standard stock solution to 100 mLs with Ultra Pure DI in a class A volumetric flask, TV = 0.25 mg/L. Prepare fresh daily or as needed.

9.8. Matrix Spikes:

The matrix spikes are prepared by measuring the volume of sample to be spiked and adding a volume of 1000 ppm standard stock to the sample to make a true value of 10.0 mg/L. (i.e. A 42 mL sample will require 0.42 mLs of 1000 ppm stock). For low level analysis spike to a true value of 0.25 mg/L.

9.9. Standards Preparation General Information and Disclaimers

9.9.1. All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 ppb standard may be made by adding 1 uL of 200 ppb to 10 mLs or may be made by adding 4 uL of 50 ppb to 10 mLs. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

9.9.2. The initial calibration curves given are typical, but also subject to variation due to targets and detection levels needed. The lowest concentration level shall be at the method reporting level. The remaining levels should define the working linear range of the analytical system.

9.9.3. All Standards must be traceable using the CAS lot system (ADM-DATANTRY).

9.10. Potassium Biphthalate (KHP) – purchased commercially. Dry to a constant weight at 103-105 °C. Allow to cool and store at room temperature in a desiccator. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.11. KHP stock solutions:

9.11.1. Standard Stock Solution (1000 ppm C): Stock solution is prepared by adding 2.128 g of KHP into a 1000 mL volumetric flask. Dilute to volume with Ultra Pure DI. Store in amber glass at room temperature for up to 1 year.

9.11.2. Reference Stock Solution (1000 ppm C): Stock solution is prepared by adding 2.128 g of KHP from a different manufacturer than the standard stock was prepared into a 1000 mL volumetric flask. Dilute to volume with Ultra Pure DI. Store in amber glass at room temperature for up to 1 year.

9.12. Calibration Standards

** Note: When using an adjustable pipette, record the pipette ID of the pipette used.

9.12.1. Prepare high level curve check standards with Ultra Pure DI as follows:

Concentration	mLs 1000 ppm Standard Stock	Final Volume
0.0	0.0	100
1.0	0.100	100
5.0	0.5	100

10.0	1.0	100
30.0	3.0	100

9.12.2. Prepare low level curve check standards with Ultra Pure DI as follows:

Concentration	μLs 1000 ppm Standard Stock	Final Volume
0.00	0	100
0.05	10.0 mLs of 0.5 Std	100
0.10	10.0 mLs of 1.0 Std	100
0.50	50	100
1.00	100	100

9.13. Gas Service: Nitrogen

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

11. PROCEDURE

11.1. Be sure the analyst has a current Demonstration of Capability and the system has a current MDL.

11.2. Turn on the nitrogen gas flow and confirm 50 - 60 psi delivery pressure. Maintain this delivery pressure. If pressure drops to below 15 psi, the instrument will automatically shut down.

11.3. Initial Power Up:

11.4. Turn on the power using the main POWER switch, boot up the WinTOC software from the desktop icon, enter your login ID and password.

11.5. Reagents

11.5.1. Confirm that acid and oxidant lines are properly positioned in reagent bottles.

11.5.2. Confirm that purge lines are placed in reagent bottles and solutions are being purged.

11.5.3. Confirm that the DI water flask is full and is being purged.

11.6. WinTOC Software:

11.6.1. Upon booting up, the WinTOC software opens to a security prompt. Enter your previously defined user name and password. After pressing enter, the Status Screen appears, which displays real-time conditions and settings for the Model 1010 analyzer.

11.6.2. Click **Setup, Configuration** and confirm that the desired analysis mode is properly selected as TOC. Ensure that the correct loop size is chosen for the correct TOC level: 1.0 mL loop for 1 - 30 ppm TOC, 10 mL loop for 0.05 to 1.0 ppm TOC. Autosampler option is the 53 vial tray, Sample Needle Depth is set for 82% for regular level TOC's, so as to avoid sediment in the bottom of VOA vials. Change depth to 95% for all low level work. Click **Advanced** to adjust key parameters for low level work, use defaults for regular levels.

11.6.3. Click **Setup, WinTOC Output** and enter today's date under the Subdirectory and as the Log File Name, and the month and day as the Prefix (e.g.: 0320) and set the Counter to 1. Presently, keep Report to Screen marked, and all Run Log Header Options as "Full". Click **OK.**

11.6.4. **Setup, Preferences**. Set default settings to 4 reps per sample for quadruplicates, 2 for duplicates and 1 for single injection. Sample volume is defined by the sample loop installed.

11.6.5. Click **Databases, Methods**. This section defines reagent and rinse volumes, and reaction times. Currently, regular level TOC's are using method "TOC1", and low-levels are using "TOC-LL". For routine analyses, the oxidant volume is set at 1000 uL, and the acid volume is 200 uL.

11.6.6. Click **Databases, Sequences**. A sequence, or schedule, is required to start any analysis. Sequences are reusable (a "template" for duplicates and quads exists, with CCV's, CCB's and LCS already scheduled in their correct order, to make long runs easier to schedule). Each schedule line must be filled in with the appropriate information for Sample Name, Method, Run Type (Sample or Cal. Standard), Reps, Dilution Factor, Volume (determined by sample loop size) and Reagent Blanks Before (default is zero. Only use this under the "Monday Blanks" sequence). Save daily sequences as the days date, mmddyy. Besides "Monday Blanks", a sequence "Daily Blanks" exists which can be used to warm up the analyzer after it has sat idle overnight.

11.7. Initial Calibration

11.7.1. The instrument subtracts a reagent blank value from each of the samples before the results are printed. To determine the reagent blank value, run the "Monday Blanks" sequence, and the average mV response of the last 5 replicates will be automatically entered into the software for this purpose.

11.7.2. Click **Instrument, Calibration**. Click "New" to start a new calibration. Define the 5 standard concentrations to be used in the calibration (the instrument software only allows 4 standards and a blank), Volume=loop volume, Cal. Mode = TOC, Allow Editing = No, RF Calculation = Automatic. All other fields are filled in automatically during the calibration. Save the calibration as "Caldate", i.e. "Calmmddyy".

11.7.3. Open the sequence screen, **Databases, Sequences**. Define the standards: Sample Name = Std 1, TV = xxxx, Method = yyyy, Run Type = Std 1, Reps = 3, Dilution factor =1, Volume = loop volume, Reagent blanks = 0. Enter all 5 standards, incrementing each name and run type appropriately. Schedule the ICV, ICB and LCS and any samples as per the standards, except that Run Type = Sample. Save the calibration sequence as the day's date (mmddyy). Print out the sequence. Note: ideally, though not necessary, only schedule the standards to run on the sequence initially, so that after the standards are run the analyst can view the curve for compliance. Otherwise, the curve will be generated and will go right into the ICV/ICB/LCS and samples.

11.7.4. Click **Instrument, Diagnostics**. Spiral the tray outwards. Remove the cover, remove the plastic rack, load the samples according to the sequence print-out. Replace the plastic rack on the metal tray (correctly line up the center spindle and outer peg). Click "Spiral tray" to return the tray to the interior. After movement of the tray has stopped, click "Go to First Vial" and ascertain that the first vial is correctly aligned below the needle port. If not, calibrate the tray as per above in the Routine Maintenance section. Click "OK" to get out of the Diagnostics screen.

11.7.5. Click **Start** to begin the calibration. A pop-up menu will ask that you confirm that the sequence loaded is to be run from position 1 to position "x" as defined in the loaded sequence. Click "OK" to start.

11.7.6. The initial calibration curve is by Linear Regression. This method of quantitation uses the equation of a line ($y=mx+b$). The curve must not be forced through zero. The correlation coefficient must be 0.997 or greater to use the curve to quantitate sample results. If it is not, determine the problem and recalibrate.

11.7.7. The calibration is confirmed with every run by the CCV, CCB, and LCS.

Daily, every run is started with a CCV, CCB, and LCS and is closed with a CCV, CCB, as well as a CCV/CCB set every 10 samples and an LCS every 20. The instrument only needs recalibration when these QC become unacceptable, or at least once a year.

11.7.8. After the calibration has finished, view and print out the calibration graph: **Utilities, Reporting, Analysis, Open Calibration, 1010,** choose the applicable calibration**, File, Print.** Statistics are printed out with the results; See the TOC Reporter section, below.

11.7.9. Consult pg. 34-36 of the WinTOC software manual for further calibration information.

11.8. Daily Sample Analysis and Continuing Calibration Verification

11.8.1. Daily set-up is the same as for the calibration, except that standards need not be run until required. Samples analyzed under Method 9060 shall be analyzed in quadruplicate, unless other client-specific requirements are approved. Samples analyzed using the 1 mL sample loop should be analyzed in duplicate to monitor the possibility of carryover. Samples analyzed using the 10 mL loop should be analyzed as a single injection.

11.8.2. If the instrument has not analyzed a sample for more than an hour, blanks must be run to reestablish baseline. Make sure at least 4 consecutive blanks are below the PQL. Use the "Daily Blanks" sequence for this purpose.

11.8.3. Daily sequences are created as per above. Ideally, and especially for quadruplicates, schedule the required QC on a StarLIMS run prior to making up the sequence. Place the Order Number for each of the QC locations in the "Sample Name" followed by the QC type. For example, the beginning of a sequences Sample Names may look like: 625100 CCV, 625101 CCB, 625102 LCS. During data export/downloading to StarLIMS, the QC data will also be downloaded and won't need to be manually entered. However, be sure that the correct QC true value is entered on the StarLIMS run; the default is 10 mg/L.

11.8.4. Load the samples into the Autosampler vial rack, starting with a CCV, CCB, LCS (in that order). Load up to 10 samples, CCV, CCB, up to 10 more samples, CCV, CCB, up to 10 more samples, etc. Make sure there is an LCS, a matrix duplicate and a matrix spike every 20 samples. Always end the run with a CCV, CCB. The CCVs and LCSs are used to verify the calibration. If dilutions are needed, make in accordance with SOP ADM-DIL.

11.9. TOC Reporter Module:

11.9.1. Results are automatically printed to a file, as defined in the "WinTOC Preferences" screen under **Setup**, one page per sample.

11.9.2. Click **Utilities, Reporting**. At the security prompt enter your previously defined user name and password Click **File, Open, Data10** and choose the subdirectory named previously in the "WinTOC Output" section of "Setup". Double click to view all the files in the directory, highlight the first 20 files, click "OK". If there are more than 20 files to be printed/exported, click "OK", **File, Open, Data10, subdirectory**, and choose the next 20 files, click "OK". Continue this until all files are loaded into this "1010 Statistics" screen.

11.9.3. Click "Print". A new menu pops up: "Header", "Footer" and "Results". Click "Results". Choose "Sample Info" and "TOC Results" for a paper print-out or to export data or to get calibration statistics. Click "Run Report". The software should go to the "OI Report Viewer" screen. Click the printer icon to print a hard copy. Click the envelope icon to export data: change the "Format" to "Text", leave the Destination File as "Disk File", Click "OK", choose the directory and file J:\Transfer\ Toc_xf\Toc2tran for duplicates, Toc4tran for quads. Click "Save", "Yes" to overwrite the file.

11.9.4. When done printing and/or exporting files, close "OI Report Viewer", close "Report Viewer", click "OK" at "1010 Statistics", close "File" to exit TOC Reporter.

12. QA/QC REQUIREMENTS

12.1. An LCS must be analyzed with each batch of 20 or fewer samples. Results must be within the limits set in Appendix C of the Quality Assurance Manual. If it is not, fix the problem, achieve an acceptable LCS and reanalyze the affected samples.

12.2. A CCV must be analyzed following every tenth sample and at the end of the run. Recovery must be within 15% of the value (85-115%). If it is not, fix the problem, achieve an acceptable CCV/CCB set and reanalyze the affected samples. Recalibrate if necessary.

12.3. A CCB must be analyzed following every CCV. The result must be below the reporting limit (*See DOD Summary, if applicable). If it is not, fix the problem, achieve an acceptable CCV/CCB set and reanalyze the affected samples.

12.4. Duplicates- One sample per 10 samples, must be analyzed in duplicate. The percent RPD for the duplicates must be < 20 %. If it is not, reanalyze the sample and DUP or flag the affected data.

12.5. Matrix Spikes- One spike sample must be analyzed per 10 samples. The matrix spike recovery should be within the limits set in Appendix C of the Quality Assurance Manual. If it is not and the LCS is in control, assume matrix interference and flag the associated data.

13. DATA REDUCTION AND REPORTING

13.1. Calculations

13.1.1. Both the mV response and the concentration are automatically printed to a file as defined in the "WinTOC Output" section.

13.1.2. The WinTOC software that acquires the instrument data multiplies the instrument's calculation by the dilution of the sample, when the dilution information is entered by the analyst in the "dilution factor" field of the Sequence. However, the current StarLIMS configuration for TOC also multiplies the dilution factor by the raw sample result. If data is downloaded to StarLIMS, the final result then appears to be the post-dilution result multiplied again by the dilution factor (i.e., a sample is run at a 1/10 dilution and the final result in the WinTOC Reporter output is 100 ppm, when the data is downloaded to StarLIMS the dilution factor will be 10, the result field will read 100 ppm and the final result on the StarLIMS report will be 1000 ppm, when in reality the actual result should be reported as 100 ppm). To prevent this from happening during data export, currently the analyst should leave the dilution factor defaulted to 1, and enter the actual dilution factor in the "Comments" section of the Sequence. During the data export, StarLIMS is programmed to pick out the dilution factor from the Comments section so that the correct result is reported.

13.2. Preliminary results are reviewed to determine if dilutions are adequate. The linear range for high level is 1.0 - 30.0 ppm. The linear range for low level is 0.05 - 1.0 ppm

13.3. Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

13.4. All sample data and QC data, including calibration verification must reference the name (date or filename) of the ICAL on the raw data report.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

Demonstration of Capability is performed upon instrument set-up , whenever a new analyst begins independent analysis, and annually thereafter according to ADM-TRANDOC and section 19 below. The documentation of this method performance is retained by the Quality Assurance office

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

Reagents are prepared upon an as-needed basis in small quantities. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

Excess, unused sample and testing byproducts are disposed following the procedures in the *SMO- SPLDIS*.

16. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. U.S. Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, Revised 1983, Method 415.1.

18.2. U.S. Environmental Protection Agency, *Total Organic Carbon*, Method 9060, SW-846 Third Edition, September 1986

18.3. OI Analytical, *WinTOC Version 5.01, Control Software for the Model 1010 TOC Analyzer*, Revision 6.3, June 2002

18.4. OI Analytical, *Model 1010 Wet Oxidation TOC Analyzer Operator's Manual*, Revision 9.1, June 2001

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2. Observe Sample Preparation and Analysis. Follow Generic Training Plan Form. Form (May be found on the Rochester CASLAB Intranet at P:\INTRANET\QAQC\TRAINING\QAforms.HTM.)

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Perform the analysis independently and show Initial Demonstration of Capability (IDC) by analyzing 4 replicates of a known mid-range standard in succession before client samples are analyzed. If recovery is within acceptable limits, complete IDC certificate and Training Plan Form and file with QA. Continuing Demonstration of Capability (CDC) will be demonstrated annually using a PE sample, single blind, or a new 4 replicate study. Demonstrate Competency by performing the analysis independently.

20. METHOD MODIFICATIONS

None

21. INSTRUMENT-SPECIFIC ADDENDUM

The instrument manual is located next to the instrument. Refer to this manual for instrument setting or specifications not described in this SOP.

22. ATTACHMENTS

- Example printout of WinTOC Analytical Sequence report
- Example printout of WinTOC Result file report.

23. CHANGES FROM PREVIOUS REVISION

- Eliminated reference to an ultra low level curve. The low level curve was changed from 0.1 – 3.0 ppm to 0.05 to 1.0 ppm using a 10 mL loop. The 25 mL loop is no longer used.
- The ICV/CCV (9.8) for the low level curve was changed from 0.5 to 0.75 ppm.
- The LCS (9.9) and MS (9.10) for the low level curve was changed from 0.05 to 0.25 ppm.
- Explanation was added regarding when the samples are to be analyzed in quadruplicate, duplicate, and by single injection in 11.7.1
- Added Definitions (Section 3) for MDL, MRL, RPD, and Initial Calibration. Referenced ADM-BATCH and re-arranged some definition orders.
- Added section for carryover in Interferences (4)
- Expanded upon Safety (5)
- Expanded upon Maintenance Log (8)

- Added Standards prep Info and Disclaimers (9)
- Added check for DOC, MDL (11)
- Added linear regression info and acceptance criteria and corrective action for ICAL (11).
- Added that the ICAL must be referenced on raw data sample reports (13)
- Expanded upon Method Performance (14)
- Added link to Training Plan Forms (19)
- Added DOD Attachment

Page 1 of 1

```
***********************************************************************
**                              SEQUENCE                             **
***********************************************************************
```

032503 Tue Mar 25 14:09:08 2003

Pos/ Vial	Sample Name	Method	Run Type	# Rep	Vol (mL)	# Blk	Dil Fact	Ovr Rng	Remarks
1	CCV	toc1	Sample	4	1.000	0	1.00	No	
2	CCB	toc1	Sample	4	1.000	0	1.00	No	
3	LCS	toc1	Sample	4	1.000	0	1.00	No	
4	625410 R-16023	toc1	Sample	4	1.000	0	1.00	No	10
5	625419	toc1	Sample	4	1.000	0	1.00	No	10
6	625420	toc1	Sample	4	1.000	0	1.00	No	4
7	625424	toc1	Sample	4	1.000	0	1.00	No	4
8	625425	toc1	Sample	4	1.000	0	1.00	No	10
9	625426	toc1	Sample	4	1.000	0	1.00	No	4
10	625428	toc1	Sample	4	1.000	0	1.00	No	2
11	618906 R-15664	toc1	Sample	4	1.000	0	1.00	No	
12	618906 DUP	toc1	Sample	4	1.000	0	1.00	No	
13	618906 SPK	toc1	Sample	4	1.000	0	1.00	No	
14	CCV	toc1	Sample	4	1.000	0	1.00	No	
15	CCB	toc1	Sample	4	1.000	0	1.00	No	
16	618907	toc1	Sample	4	1.000	0	1.00	No	
17	618908	toc1	Sample	4	1.000	0	1.00	No	
18	618909	toc1	Sample	4	1.000	0	1.00	No	
19	618910	toc1	Sample	4	1.000	0	1.00	No	
20	618911	toc1	Sample	4	1.000	0	1.00	No	
21	618912	toc1	Sample	4	1.000	0	1.00	No	
22	618913	toc1	Sample	4	1.000	0	1.00	No	
23	618914	toc1	Sample	4	1.000	0	1.00	No	
24	618915	toc1	Sample	4	1.000	0	1.00	No	
25	618916	toc1	Sample	4	1.000	0	1.00	No	
26	CCV	toc1	Sample	4	1.000	0	1.00	No	
27	CCB	toc1	Sample	4	1.000	0	1.00	No	
28	LCS	toc1	Sample	4	1.000	0	1.00	No	
29	618916 DUP	toc1	Sample	4	1.000	0	1.00	No	
30	618916 SPK	toc1	Sample	4	1.000	0	1.00	No	
31	618917	toc1	Sample	4	1.000	0	1.00	No	
32	618918	toc1	Sample	4	1.000	0	1.00	No	
33	CCV	toc1	Sample	4	1.000	0	1.00	No	
34	CCB	toc1	Sample	4	1.000	0	1.00	No	

pipets: TOC/TOX
wayne

1 Mustard Street
Rochester, NY. 14609
585-288-5380

OI Analytical Model 1010

Sample Information:

Sample #:	1	Operator Name:	TWARNER	Method Name:	toc1
Sample Name:	628158 CCV	Sample Volume (ml):	1.025	Sequence Name:	032503
Run Type:	SAMPLE	Loop Volume (ml):	1.025	Calibration Name:	cal010903
Analysis Mode:	TOC	Loop Size (ml):	1.000	PAM Mode:	OFF
Total Reps:	4	Sample Intro:	AUTOSAMPLER	PAM Volume (ul):	0
Date:	25Mar2003	Remote Start:	OFF	PAM Purge (min:sec):	0:30
Dilution Factor:	1.00	File Name:	0325005.rlt		
Comments:					

Sample Results:

Rep #	Time	TOC Area (cnts)	TOC Mass (ugC)	TOC Conc (ppm)
1	14:27	16990	18.804	18.345
2	14:36	16394	18.135	17.692
3	14:45	18182	20.143	19.652
4	14:55	18213	20.178	19.685

OL 3/26/03

'*' = modified '~' = unused

Report generrated by OI Analytical's TOC Reporter V5.0, using WinToc 1010 V5.0 and 1010 Firmware V5.0

*DOD SUMMARY

For work for the Department of Defense – the DOD Quality Systems Manual must be followed. The DOD Manual is based on the NELAC Standards with some additional requirements. The following are the requirements which are different or additional to routine analysis and must be followed for DOD work:

- The Method Blank must not have any hits above ½ the reporting limit.

- Reporting Limits – “The lower quantitation limit is established by the low standard of the initial calibration curve or the low-level calibration check standard. At a minimum the quantitation limit shall be three times the detection limit”. DoD QSM, V2, Clarification D-13

STANDARD OPERATING PROCEDURE

DETERMINATION OF SULFIDES BY DISTILLATION AND IODIMETRIC TITRATION

GEN-9030B/9034

Revision 1
May 21, 2001

Approved By:	______________________	__________
	Supervisor	Date
	______________________	__________
	QA Coordinator	Date
	______________________	__________
	Laboratory Manager	Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: ________

1 SCOPE AND APPLICATION

1.1 This procedure is designed for the determination of sulfide in aqueous, solid waste materials, or effluents using SW846 Method 9030B/9034. This procedure is suitable for measuring sulfide concentrations in the range of 0.2-50ppm.

1.2 This method is not applicable to oil or multiphasic samples.

1.3 This method measures total sulfide which is usually defined as the acid-soluble fraction of a waste. Although Method 9030B covers the determination of acid-insoluble sulfides, this SOP does not.

2 METHOD SUMMARY

The sample is distilled under acidic conditions at 70°C under a stream of nitrogen. Hydrogen sulfide is released and collected in gas scrubbing bottles containing zinc(II) and a strong acetate buffer. Zinc sulfide precipitates and is measured by iodimetric titration.

3 DEFINITIONS

3.1 **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of standard solution of the analyte is added to a sample matrix prior to sample distillation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analyte detected.

3.2 **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.3 **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.4 **Laboratory Control Sample (LCS)** - In the LCS or blank spike analysis, a predetermined quantity of standard solution of the analyte is added to a blank prior to sample distillation and analysis. Percent recovery is calculated for the analyte detected.

4 INTERFERENCES

4.1 Aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

4.2 Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may carry over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine in the determinative step to yield false high values. The addition of formaldehyde into the scrubber removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferent.

5 SAFETY

5.1 Sulfide gas (H_2S) is highly toxic. Care must be taken with the samples and when preparing references. The threshold odor concentration in clean water is between 0.025 and 0.25 µg/L.

5.2 Formaldehyde and sulfuric acid should be handled with care.

5.3 Lab coat, glasses, and gloves should be worn when performing this test.

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1 Aqueous samples are collected with a minimum of aeration in 300 mL glass BOD bottles or 500 mL certified clean plastic bottles, preserved with 2.0 mLs of 2N zinc acetate and 2-3 pellets of sodium hydroxide. Fill to no headspace and cap tightly. Store at 0-6°C until analysis.

6.2 Soil samples are to be collected in glass jars with no headspace. Store at 0-6°C until analysis.

6.3 Samples are to be analyzed within 7 days of collection.

6.4 Further sample handling, storage, and custody procedures are discussed in SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 See Figures 1 and 2 for Apparatus Configuration

7.2 Midi Distillation Unit (Midi Vap Model MCV 103), if using Midi.

7.3 Distillation tubes (Midi) or flasks (Macro).

7.4 Distillation heads with fritted outlet.

7.5 Absorber (scrubber) tubes.

7.6 Absorber (scrubber) heads with fritted outlet.

7.7 Dropping funnel with stopcock and pressure equalizing arm.

7.8 1/4 inch tubing and quick disconnects.

7.9 Nitrogen source and gas tubing.

7.10 Common laboratory glassware and equipment including 500 mL Erlenmeyer flasks, graduated cylinders, stir plate with stir bars, 10 mL buret with 0.05 mL increments, pipettes, DI bottle, calibrated top loading balance, calibrated analytical balance, calibrated micropipettor, and volumetric flasks.

8 PREVENTIVE MAINTENANCE

8.1 Check all connections on the apparatus for leaks by wetting connections with a weak soap solution and looking for bubbles.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Concentrated Hydrochloric Acid – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.2 6N Hydrochloric Acid - Carefully add 100 mL of concentrated HCl to 100 mL of DI. Store at room temperature in plastic for up to 1 year.

9.3 Potassium iodide (KI) – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.4 Iodine – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.5 Standard iodine solution (0.0250N) - Add 20 - 25 g KI to 50 mL DI and mix. Add 3.2 g iodine. Dilute volumetrically to 1 Liter with DI. Store in amber glass at 0-6°C for up to 1 year. Standardize with each use against 0.0250N $Na_2S_2O_3$ as follows:

9.5.1 Volumetrically place 5.0 mL iodine solution in a small beaker or Erlenmeyer flask.
9.5.2 Titrate with 0.025 N $Na_2S_2O_3$ to a light yellow.
9.5.3 Add approximately 0.5 mL starch indicator.
9.5.4 Continue titrating to colorless.
9.5.5 Calculate the actual normality of the iodine solution:

$$\text{Normality of Iodine} = \frac{(\text{Volume(mLs) of } Na_2S_2O_3)(\text{Normality of } Na_2S_2O_3)}{(\text{Volume of Iodine(mLs)})}$$

9.5.6 Record standardization in standardization log book

9.6 Standard potassium bi-iodate solution (0.025N) - Add 0.81225g $KH(IO_3)_2$ to 800 mL DI in a 1 L volumetric flask and dissolve. Dilute to mark. Prepare fresh daily as needed for standardization of $Na_2S_2O_3$.

9.7 Standard sodium thiosulfate solution (0.0250N) - Dilute commercially prepared stock as necessary. Prepare fresh every 14 days or standardize as follows:

9.7.1 Dissolve approximately 2 g KI in 100 mL DI.
9.7.2 Add 1 mL 6N HCl.
9.7.3 Add 9 mL standard bi-iodate solution.
9.7.4 Dilute to 200 mL, add starch indicator and titrate to colorless with sodium thiosulfate solution.
9.7.5 Calculate the normality of the solution as follows:

$$\text{Normality of } Na_2S_2O_3 = \frac{(\text{Volume of } KH(IO_3)_2\text{(mLs)})(\text{Normality of } KH(IO_3)_2)}{\text{Volume of } Na_2S_2O_3\text{(mLs)}}$$

9.8 Starch Indicator - Purchased commercially. Store at 0-6°C in plastic. Expires upon manufacturer's indications, one year from receipt, or when it no longer produces the intended indication effect, whichever is sooner.

9.9 Zinc Acetate ($Zn(C_2H_3O_2) \bullet 2H_2O$) – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.10 Zinc Acetate Preservative (2N)- Add 220 g $Zn(C_2H_3O_2) \bullet 2H_2O$ to 800 mL DI and mix. Dilute to 1 Liter. Store at 0-6°C in amber glass for up to 1 year.

9.11 Zinc Acetate Stock (0.5M) - Add 110 g $Zn(C_2H_3O_2)\bullet 2H_2O$ to 800 mL DI and mix. Add 1 mL 6N HCl to prevent the formation of zinc hydroxide and dilute to 1 Liter. Store at 0-6°C in amber glass for up to 1 year.

9.12 Formaldehyde (35-40%) - Purchased commercially. Store in flammable cabinet. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.13 Concentrated, reagent grade sulfuric acid - Purchased commercially.

9.14 Sodium Sulfide crystals ($Na_2S\bullet 9H_2O$) – purchased commercially. Store tightly capped at 0-6 °C. Expires upon manufacturer's indications or 3 years from receipt, whichever is sooner.

9.15 Sulfide reference solution - Weigh approximately 0.4 g $Na_2S\bullet 9H_2O$ on the analytical balance and record the actual weight. Add the sodium sulfide to a tared glass bottle and dilute to 100g with DI. Store at 0-6°C for up to 1 week. Calculate the concentration of the solution as follows:

$$\text{mg/mL } S^{2-} = \frac{(\text{g } Na_2S\bullet 9H_2O)(0.1333)}{\text{Final Volume(mLs)}} \times \frac{1000\text{mg}}{\text{g}}$$

9.15.1 Standardization of the Sulfide Reference Solution – Pipet 5.0 mLs 0.025N standardized iodine solution into a 250 mL Erlenmeyer flask. Add 100 mLs DI and 2 mLs 1:1 HCl. Add 2 mLs sulfide reference solution to 100 mLs DI and titrate with 0.025N $Na_2S_2O_3$ to a light yellow. Add 1 mL starch and titrate to clear. Calculate as in the sample calculation. Record standardization in standardization log book.

9.16 LCS/MS - Midi -Add 2.0 mL of the sulfide reference solution to 100 mL DI (or sample) or 6 g Ottawa sand (or sample) in the distillation tube.

9.17 LCS/MS - Macro - Add 2.0 mL of the sulfide reference solution to 100 mL DI (or sample) or 10 g Ottawa sand (or sample) in the distillation flask.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURE

11.1 Sample Preparation

11.1.1 Check and record the pH of the sample. Homogenize sample and measure into sample tube or flask, recording actual weight or volume. Use 10 g or 100 mL for Macro distillation. Use 6 g or 100 mL for Midi distillation. In order to prevent blocking of the distillation head's fritted end and maintain fluid motion, it may be necessary to further limit the mass for the Midi distillation if the sample is porous and will swell in water.

11.1.2 For non-aqueous samples, add an additional 50 mL DI to the sample tube (midi) or 250 mL DI to the sample flask (Macro).

11.2 Apparatus Preparation

11.2.1 The midi distillation unit should be assembled as in Figure 1.
11.2.2 The macro distillation should be assembled as in Figure 2.

11.3 Distillation Procedure

11.3.1 In the scrubber tube, place 20 mL 0.5 M ZnAcetate, 10 mL Formaldehyde, and 50 mL DI.

11.3.2 Assemble system

11.3.3 Place 25 mL (midi) or 75 mL (macro) concentrated sulfuric acid in the dropping funnel.

11.3.4 Turn on Nitrogen gas and adjust delivery to individual scrubbers to about 25 mL gas/ min. Limit the pressure to about 10 psi to prevent excess stress on the glass system and fittings. Purge system for at least 5 minutes. Check for leaks with a diluted soap solution.

11.3.5 Heat system to 70°C.

11.3.6 Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until all of the acid has entered the flask. *CAUTION: Violent reactions and foaming can occur*.

11.3.7 Maintain heat and purge for 90 minutes.

11.3.8 Turn off heat and nitrogen supply.

11.4 Preparation of distilled sample for analysis

11.4.1 Check the pH of the distilled sample. pH should be <1. If the pH is not <1, incomplete distillation may have occurred and the sample should be redistilled at a lesser volume.

11.4.2 Prepare the rinse solution as follows:

11.4.2.1 With a volumetric pipette, place 5.0 mL iodine solution in a 100 mL flask.
11.4.2.2 Add approximately 50 mL DI.
11.4.2.3 Add 2.0 mL 6N HCl.
11.4.2.4 Dilute to approximately 100 mL with DI

11.4.3 Disassemble, pour scrubber solution into a 500 mL Erlenmeyer flask with a minimum of aeration.

11.4.4 Carefully rinse the scrubber tube and head with the rinse solution, being sure to rinse the inside of the fritted end. Do not spill any of this rinse. Collect all the rinseate in the 500 mL Erlenmeyer with the sample. Rinse again with DI and collect rinseate in the 500 mL Erlenmeyer. Pour any remaining rinse solution into the Erlenmeyer for titrimetric analysis.

11.5 Iodimetric Titration Analysis

11.5.1 If the orange color of the iodine disappears, add additional measured portions of iodine solution until the orange color persists. Record total volume of iodine solution used on the benchsheet.

11.5.2 Titrate all rinses and scrubber solution with 0.0250N $Na_2S_2O_3$ to a light yellow.

11.5.3 Add 1 mL starch. Solution will turn blue.

11.5.4 Continue titrating until blue color disappears. Record on the benchsheet the volume of $Na_2S_2O_3$ needed to reach endpoint.

12 QA/QC REQUIREMENTS

12.1 One blank must be analyzed per batch of 20 or fewer samples. The result of the blank must be less than the detection limit. Positive detections indicate possible laboratory contamination and the batch should be redistilled and reanalyzed.

12.2 One sample must be analyzed in duplicate for every batch of 20 or fewer samples, volume permitting. The %RPD must be less than 20% for samples greater than 5 times the PQL. For samples less than 5 times the PQL, the duplicate must be within the value of the sample +/- the PQL. Poor precision may indicate matrix interferences and these data may be flagged as estimated.

12.3 One spiked sample must be analyzed for every batch of 20 or fewer samples, volume permitting. The % recovery must be within the limits in the Wetchem QC table in the Quality Assurance Manual. Outlying recoveries may indicate matrix interferences and these data may be flagged as estimated. Evaluate the LCS to determine reanalysis.

12.4 One LCS must be analyzed for every batch of 20 or fewer samples. The % recovery must be within the limits in the Wetchem QC table in the Quality Assurance Manual. Outlying recoveries indicate inaccurate distillation or analysis procedures and the batch should be redistilled and reanalyzed.

12.5 An MDL study must be performed annually. The result of the study must be less than the reporting limit. If it is not, fix the problem and repeat the study or raise the reporting limit. For more information, see ADM-MDL.

13 DATA REDUCTION AND REPORTING

13.1 Calculations

$$\text{Sulfide (mg/L or mg/Kg)} = \frac{(A \times B) - (C \times D)}{\text{L or Kg}} \times 16.03$$

Where: A = volume(mL) iodine used
B = Normality of iodine solution
C = Volume (mL) sodium thiosulfate used
D = Normality of sodium thiosulfate

13.2 Data review policies and procedures are in ADM-DREV.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis. Acidic waste is neutralized and poured down the drain with copious amounts of water. For more information see SMO-SPLDIS.

15 REFERENCES

15.1 *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, USEPA SW-846, December 1996.

16 TRAINING OUTLINE

16.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

16.2 Observe Sample Preparation and Analysis. Follow distillation and titration Training Plan Forms.

16.3 Participate in the methodology, documentation, and data reduction with guidance.

16.4 Demonstrate Initial Competency (IDC) by performing the analysis independently. Analyze four replicates of a known mid-range standard. If recovery is within acceptable limits, complete Training Plan Forms and IDC certificate and file with QA. Continuing Demonstration of Capability (CDC) will be demonstrated annually using a PE, single blind, or a new four replicate study.

17 INSTRUMENT-SPECIFIC ADDENDUM

None

18 ATTACHMENTS

18.1 Figure 1: Midi Apparatus

18.2 Figure 2: Macro Apparatus

19 CHANGES FROM PREVIOUS REVISION

19.1 Added the method number to 1.0.
19.2 Added references to SMO-GEN, ADM-MDL, ADM-DREV, ADM-TRANDOC, and SMO-SPLDIS.
19.3 Removed need to add zinc acetate as a preservative of soils.
19.4 Split out some purchased reagents from prepared solutions.
19.5 Added 500 mL plastic bottles to 6.0.
19.6 Changed listed QC limits to a reference to the Wetchem QC table in the Quality Assurance Manual.
19.7 Explained that the method covers acid-insoluble sulfides but this SOP does not.
19.8 Eliminated interference by tin(II) Chloride since it is not added.
19.9 Added need to check and record the preservation of the sample.
19.10 Changed preservation of sample from 1 small pellet of NaOH to 2-3 pellets.
19.11 Added standardization of sulfide reference solution.
19.12 Added need to record distillations in distillation log book.
19.13 Changed from adding 5.0 mL aliquots in 11.5.1 to “measured” aliquots.

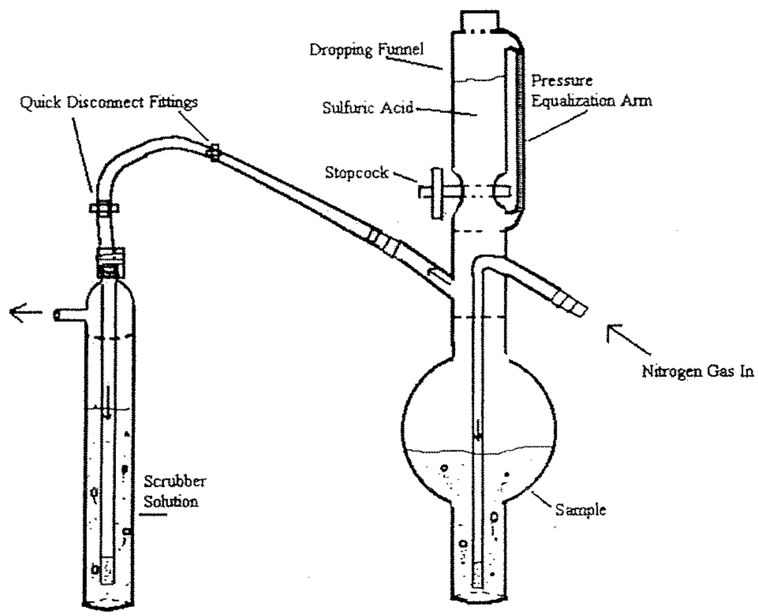
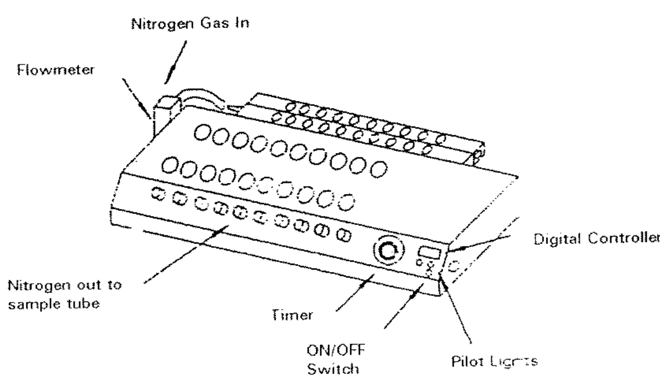


FIGURE 1: GAS EVOLUTION APPARATUS FOR MIDI DISTILLATION



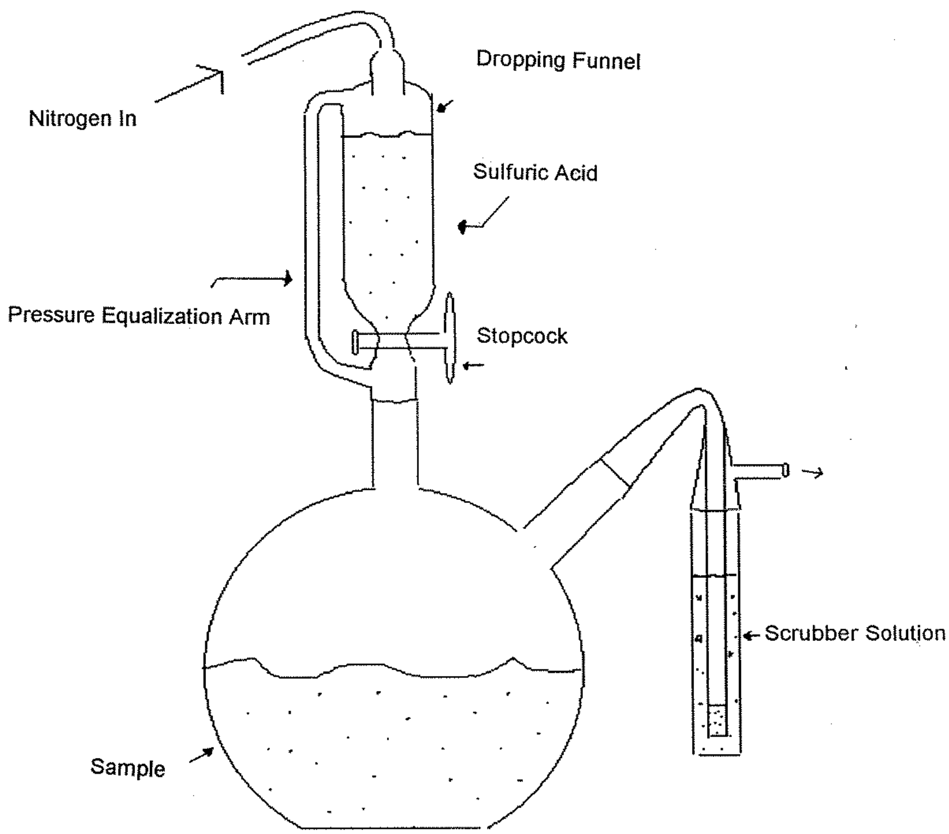


FIGURE 2: GAS EVOLUTION APPARATUS FOR MACRO DISTILLATION

Columbia Analytical Services
1 Mustard Street
Rochester, NY 14609
(716) 288-5380

Analyst:______________________
Date:____________ Time:_________
Pipet ID:______________

Total Sulfide SW846, Method 9030B

Iodine Solution (N):________________ Prep:________________ Stnd'n:________________
Sodium Thio (N):________________ Prep:________________ Stnd'n:________________
Sulfide Ref (mg/L):________________ Prep:________________ Stnd'n:________________

Sub #	Order #	Preservation Check	Distillation pH Check	Distilled vol. (Kg or L)	Na-Thio Titrant (mLs)	I2 (mLs)	Total Sulfide (mg/L)

Sulfide, mg/L or mg/Kg = 16.03[(AxB) - (CxD) / L or Kg Sample]

where: A = volume (mL) of Iodine solution used
B = Normality of Iodine solution
C = volume (mL) of Thiosulfate solution used
D = Normality of Thiosulfate solution used

p:\Lotus\123r22\greg\forms\benchsheet\9030B

STANDARD OPERATING PROCEDURE

COLORIMETRIC DETERMINIATION OF SILICA IN WATER

GEN-370.1

Revision 1
June 12, 2001

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL
NUMBER: ________________
Initials: ______ Date: ________

1 SCOPE AND APPLICATION

1.1 This SOP uses EPA method 370.1 for colorimetric determination of dissolved silica (SiO_2).

1.2 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.3 The normal reporting limit is 0.010 mg/L SiO_2/L. The range is to 1.00 and may be extended with sample dilution. Low level analysis is possible with a reporting limit of 0.004 mg/L.

2 METHOD SUMMARY

2.1 Soluble silica reacts with molybdate under acidic conditions to form a yellow silica molybdate complex. This complex is reduced with ANSA (1-amino-2-napthol-4-sulfuric acid) and bisulfate to form heteropoly blue complex with an absorbance at 820 nm.

3 DEFINITIONS

3.1 **Independent Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.2 **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of a standard solution of the analyte is added to a sample matrix prior to sample digestion and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recovery is calculated for the analyte detected.

3.3 **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.4 **Continuing Calibration Verification Standard (CCV) -** A standard analyzed at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.5 **Instrument Blank (CCB) -** The instrument blank (also called continuing calibration blank) is a volume of blank reagent of composition identical to the digestates. The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

3.6 **Laboratory Control Sample (LCS)** - An aliquot of reagent water to which a known quantity of the method analyte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.7 **Client Requested Detection Limit (CRDL)**: (Performed on QC 8000 only), The two standards of lowest concentration are included in the analytical run to show the precision of the calibration at and around the detection limit.

4 INTERFERENCES

4.1 All transfer and storage containers should be plastic to avoid contamination.

4.2 The DI water lines in the building have some Silica in them, therefore all reagents should be made with Millipore filtered water. Carrier and diluent are purchased DI water.

4.3 Phosphate interference is reduced by adding the Oxalic Acid Reagent.

4.4 Tannin and large amounts of iron or sulfides can be removed by acidifying and boiling the samples for sulfides and by adding disodium EDTA for iron.

5 SAFETY

5.1 Wear gloves, lab coat, and safety glasses when handling samples and reagents.

5.2 The toxicity and carcinogenicity of the reagents for this method have not been fully established. Each chemical should be treated as though it is a potential health hazard and exposure should be as limited as possible.

5.3 Consult the MSDS for detailed explanations of the health hazards associated with the following chemicals:

5.3.1 Sulfuric Acid

5.3.2 1-amino-2-napthanol-4-sulfonic acid (ANSA)

5.3.3 Oxalic Acid

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1 ALL CONTAINERS MUST BE PLASTIC!!!

6.2 No chemical preservative is to be used for silica.

6.3 Store samples between 0-6° C.

6.4 Analysis of samples is to occur within 28 days of sampling.

6.5 For further sample handling, storage, and custody procedures, see SMO-GEN.

7 APPARATUS AND EQUIPMENT

7.1 Micropipettor with range of 100µL-1000µL.

7.2 Analytical Balance capable of weighing to 0.1 mg.

7.3 Lachat Quickchem IV or 8000 auto analyzer with:

7.3.1 Automated sampler

7.3.2 Multichannel pump

7.3.3 Manifold or Reaction Module

7.3.4 Colorimetric Detector

7.3.5 Data recording Device (Personal Computer)

8 PREVENTIVE MAINTENANCE

8.1 Be sure to use Millipore filtered DI water for all reagents.

8.2 Be sure all equipment used is plastic including pipets, weights at end of feed lines, and reagent storage bottles.

8.3 Nearly all of the components of the Lachat can be easily cleaned or replaced. The exception is the valve. When the valve becomes clogged it is necessary to have the unit sent out to be serviced. To avoid this expense and inconvenience, be sure sample cups, and dispo cups are free of particulates by rinsing thoroughly with D.I. water and drying. Visual inspection of this equipment is also recommended before analysis. Turbid samples should also be filtered to prevent valve clogs.

8.4 Be sure to change pump tubes regularly to ensure optimal performance.

8.5 All changes in tubing, hardware, or programming are to be noted in the maintenance logbook. Record the first acceptable run in the logbook after major maintenance.

8.6 Keep the instrument and the bench area clean. Wipe down counters before and / or after use.

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 Carrier and Diluent: Because DI water lines in the building contain small amounts of Silica, the carrier and diluent are purchased Deionized Water (DI).

9.2 **Low Level Silica Standards** (0.004 mg/L - 0.100 mg/L)

A.) 10 mg/L Standard Working Stock (purchased) – store at room temperature. Expires upon manufacturer's indications or one year from receipt, whichever is sooner.

B.) Standards - store at room temperature in plastic. Exp. 1 year

conc.(mg/L)	mLs 10 mg/L	mLs Millipore DI
a.) 0.100	1.00	99.0
b.) 0.080	0.80	99.2
c.) 0.060	0.60	99.4
d.) 0.040	0.40	99.6
e.) 0.020	0.20	99.8
f.) 0.010	10 mLs of (a.)	90.0
g.) 0.006	10 mLs of (c.)	90.0
h.) 0.004	10 mLs of (d.)	90.0
i.) 0.000	0.00	100.0

C.) ICV/CCV: (True Value=0.050 mg/L)
1/200 dilution of 10 mg/L purchased Reference Stock. Prepare fresh daily.

D.) LCS/Matrix Spike: (True Value=0.025 mg/L)
10.0 mLs Millipore DI (or sample) + 0.025 mLs 10 mg/L Standard Stock. Prepare fresh daily.

9.3 **Regular Level Silica Standards** (0.010 mg/L - 1.00 mg/L)

A.) 10mg/L Standard Working Stock (purchased) – store at room temperature. Expires upon manufacturer's indications or one year from receipt, whichever is sooner.

B.) Standards – prepare fresh daily.

conc.(mg/L)	mLs 10 mg/L	mLs Millipore DI
a.) 1.000	1.000	9.00
b.) 0.500	0.500	9.50
c.) 0.200	0.200	9.80
d.) 0.100	1 mL of (a.)	9.00
e.) 0.050	1 mL of (b.)	9.00
f.) 0.020	1 mL of (c.)	9.00
g.) 0.010	1 mL of (d.)	9.00
h.) 0.000	0.00	10.0

C.) ICV/CCV: (True Value=0.75 mg/L)
9.25 mLs of Millipore DI + 0.75 mL 10 mg/L Reference Stock. Make fresh daily.

D.) LCS/Matrix Spike: (True Value=0.250 mg/L)

10 mLs of Millipore DI (or sample) + 0.250 mLs of 10 mg/L Standard Stock. Make fresh daily.

9.4 Ammonium Molybdate Tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.5 Sulfuric Acid (H_2SO_4) – concentrated - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.6 Ammonium Molybdate Color Reagent: To a tared 500 mL **Plastic** Bottle add: 243 g Millipore DI, 10.0 g Ammonium Molybdate, 7.40 g H_2SO_4. Store at 0-6 °C. Expires 1 month.

9.7 Oxalic Acid - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.8 Oxalic Acid Solution: To a tared 500 mL **Plastic** Bottle add: 490 g Millipore DI, 50.0 g Oxalic Acid. Store at Room Temperature. Expires 1 year.

9.9 Sodium Sulfite - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.10 ANSA (1-amino-2-napthol-4-sulfuric acid) - purchased commercially. Store at 0-6 °C. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.11 Sodium Bisulfite - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.12 Glycerol - purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.13 ANSA Reducing Agent: To a tared **Dark Plastic** Bottle add: 2.0 g Sodium Sulfite, 396 g Millipore DI, 0.25 g ANSA, 15.0 g Sodium Bisulfite, 5.2 g Glycerol. Store at 0-6°C. Expires 1 year.

10 RESPONSIBILITIES

10.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11 PROCEDURE

11.1 Prepare standards and reagents as described in Section 9.

11.2 Turn on the computer and Lachat components.

11.3 Connect the manifold to the instrument (see attached diagram). Inspect the manifold for proper connections, appropriate sample loop, and wavelength filter. Place pump tubes loosely in their holders.

11.4 Load the appropriate method into the software and enter sample labels for the first tray in accordance with the analytical sequence described below. The method should be optimized from the suggested operating parameters in the Lachat instrument manual. The Lachat software will calculate all dilutions provided the dilution information is entered.

11.5 Analytical Sequence:

1.	Ref (ICV)
2.	Instrument Blank (ICB)
3.	Blank Spike (LCS)
4 -13.	9 Samples
14.	Ref (CCV)
15.	Blank (CCB)
16-25.	10 Samples
26.	Ref (CCV)
27.	Blank (CCB)
28.	Blank Spike (LCS)

Analyze CRDLs on the Lachat 8000 to see the response at the low end of the curve since the software does not quantitate the standards in the calibration.

Repeat steps 4-28 until all samples are analyzed. The sequence must end with a Reference and a Blank. Insert DUP/MS where appropriate. Consult the QC section for further QC sample frequency requirements. For the QuikChem IV, it is helpful to load each tray with 20 samples and begin each tray with an LCS.

11.6 Load the calibration standards, and the samples into the autosampler as entered into the software with standards in order of decreasing concentration. Make sample dilutions in compliance with ADM-DIL.

11.7 For turbid samples or samples with particulates, filter through a syringe filter which has been shown to be free of silica and shown not to remove silica. Demonstrate these properties by analyzing a filtered blank and a filtered LCS.

11.8 Place all reagent lines in DI to rinse. Be sure waste lines go to the sink.

11.9 Attach lines to pump collars. Turn on pump. Lock in collars. Rinse for a couple of minutes. Inspect for leaks.

11.10 With pump still engaged, place the feed lines in their appropriate reagent bottles. Pump for a couple of minutes.

11.11 For the QuikChem IV, set the gain and adjust the baseline reading to about 25 mv. The QC8000 automatically sets baseline and gain.

11.12 For the QuikChem IV, position the sample tray in the autosampler so that the first standard is positioned in front of the sampler needle.

11.13 Start analysis. After the last standard has been analyzed, review the calibration data. The correlation coefficient must be 0.997 or better for the analysis to continue. A standard may be deleted from the calibration curve. If a linear curve is not achieved, stop the analysis, correct the problem, and recalibrate.

11.14 After an acceptable calibration is achieved, continue with sample analysis. Each sample must be "bracketed" by an acceptable Reference/Blank set. If a Reference or Blank fails, all samples back to the last good Ref/Blk set must be reanalyzed after the problem is corrected and a good Ref/Blk set is obtained.

11.15 For all samples in which the analyte value has exceeded the high standard, proper dilutions must be made of the sample to bring it within the range of the calibration standards.

11.16 When finished analyzing samples and QC items, place feedlines in water and rinse for 5 minutes. Remove all lines from DI and pump to dry for about 5 minutes Turn off the pump and release tension on pump tubes.

11.17 Print the results and the calibration information.

12 QA/QC REQUIREMENTS

12.1 An MDL study must be run annually. The result of the MDL must be less than the reporting limit. If it is not, correct the problem and repeat the study or raise the reporting limit. See ADM-MDL for more information.

12.2 The calibration coefficient must be 0.997 or better for analysis to continue.

12.3 <u>ICV</u> – Analyze immediately after the calibration standards. The result of the ICV must be 90-110 % of the true value. If it is not, fix the problem and recalibrate if necessary.

12.4 CCV – Analyze every 10 samples or fewer. Recovery must be 90-110% of the true value, or the bracketed samples must be repeated.

12.5 ICB/CCB - Analyze one for every 10 or fewer samples. They must be less than the reporting limit. If they are not, correct the problem and re-analyze the affected samples or raise the reporting limit.

12.6 LCS - Prepare one for every 20 or fewer field samples. LCS recovery must be within the limits in the Wetchem QC table in Appendix C of the Quality Assurance Manual. If the LCS is outside of these limits, redigest and reanalyze the affected samples or flag the affected data.

12.7 Duplicates – One duplicate must be run for every 10 or fewer field samples. The relative percent difference (RPD) between matrix duplicates should be 20 or less. If it is not, reanalyze the sample and DUP or flag the data.

12.8 Matrix Spike – One MS must be run for every 10 or fewer field samples. Matrix spike recovery must be within the limits in the Wetchem QC table in Appendix C of the Quality Assurance Manual. If it is not, reanalyze the MS or flag the data.

13 DATA REDUCTION AND REPORTING

13.1 Calibration is done by injection standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is automatically calculated from the regression equation. A minimum of 5 standards is required for a calibration curve. Selected standards may be deleted to improve correlation coefficient to above 0.997.

13.2 Report values to three significant figures in mg/L that fall between the lowest and highest calibration standards. If a sample value exceeds that of the highest standard, that sample should be diluted and reanalyzed.

13.3 Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1 Reagents are prepared upon an as-needed basis in small quantities. Minimum sample volumes are used during analysis.

14.2 Samples are disposed according to SMO-SPLDIS.

15 REFERENCES

15.1 *Determination of Silica in Waters by Flow Injection Analysis*, QuikChem Method 10-114-27-1-A, Zellweger Analytics Inc., Lachat Instruments Division, 1998.

15.2 *Methods for Chemical Analysis of Water and Wastes*, U.S. Environmental Protection Agency, EPA-600/4-79/020, Method #370.1 Rev. 3/1983.

15.3 *Standard Methods for the Examination of Water and Waste water*, 18th Ed., APHA-AWWA/WEF, Method 4500-Si F., 1992

16 TRAINING OUTLINE

16.1 Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies on ADM-TRANDOC.

16.2 Observe Sample Preparation and Analysis. Follow Lachat Training Plan Form.

16.3 Participate in the methodology, documentation, and data reduction with guidance.

16.4 Perform an IDC (Initial Demonstration of Competency) by independently analyzing four mid-range standards prior to analyzing client samples. If recovery is within acceptable limits, complete Training Plan Form and file with QA. Continuing proficiency (CDC) will be demonstrated annually using a PE, a single blind, or a new 4 replicate study. Read applicable methodologies. Demonstrate a general understanding of the methodology and chemistry.

17 INSTRUMENT-SPECIFIC ADDENDUM

17.1 See Lachat manuals located near Lachat QC 8000.

18 ATTACHMENTS

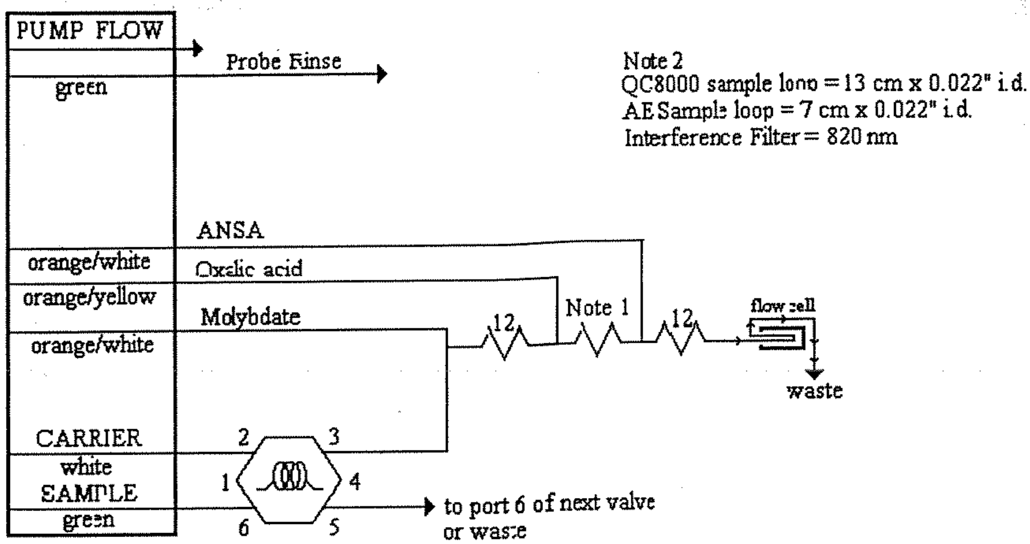
18.1 Manifold Diagram

19 CHANGES FROM PREVIOUS REVISION

19.1 Added references to ADM-MDL, ADM-DREV, ADM-TRANDOC, ADM-DIL, SMO-GEN, SMO-SPLDIS.
19.2 Split out single reagents from prepared reagents. Added storage and expiration where needed.
19.3 Modified Training Outline to reflect current practice.
19.4 Added significant amounts of detail to the Procedure to be consistent with other Lachat SOPs.
19.5 Eliminated the QC table and added information to the text in 12.0.

17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1. SILICATE MANIFOLD DIAGRAM



CARRIER is DI water.

Manifold tubing is **0.5 mm (0.022 in) i.d.** This is **2.5 µL/cm.**

12	is	**255**	cm of tubing on a 12 cm coil support
22	is	**550**	cm of tubing on a 22 cm coil support

APPARATUS: An injection valve, a 10 mm path length flow cell, and a colorimeter detector module are required.

Note 1: The manifold will come with a 12 cm coil here. This can be replaced with a 22 cm coil, which is included with a new manifold. See Interferences.

Note 2: For the AE, the tubing is connected to unions connected to valve flares. For the QC8000, the loop is connected directly to the valve.

SILICA (1.000 - 0.000 (pql=0.010))

A.) 10.0 ppm WORKING STOCK:
Purchased 10.0 ppm Standard Stock

B.) STANDARDS:

conc. (mg/l)	mls 10 ppm	mls DI
a.) 1.000	1.00	9.00
b.) 0.500	0.50	9.50
c.) 0.200	0.20	9.80
d.) 0.100	1/10 dil'n of a.) 1.000	
e.) 0.050	1/10 dil'n of b.) 0.500	
f.) 0.020	1/10 dil'n of c.) 0.200	
g.) 0.010	1/10 dil'n of d.) 0.100	
h.) 0.000	10 mls DI water	

C.) ICV / CCV: (True Value = 0.750 mg/l)
9.25 mls DI + 0.75 mls 10.0 ppm Reference Stock (purchased 10.0 ppm Ref. Stock).

D.) LCS / Matrix Spike: (True Value = 0.250 mg/l)
10.0 mls DI / sample + 0.250mls 10 ppm Standard Stock.

*** All standards, references, lcs and all dilutions are made only with bottled VWR DI!!!**

SILICA (1.000 - 0.000 (pql=0.010))

A.) 10.0 ppm WORKING STOCK:
Purchased 10.0 ppm Standard Stock

B.) STANDARDS:

conc. (mg/l)	mls 10 ppm	mls DI
a.) 1.000	1.00	9.00
b.) 0.500	0.50	9.50
c.) 0.200	0.20	9.80
d.) 0.100	1/10 dil'n of a.) 1.000	
e.) 0.050	1/10 dil'n of b.) 0.500	
f.) 0.020	1/10 dil'n of c.) 0.200	
g.) 0.010	1/10 dil'n of d.) 0.100	
h.) 0.000	10 mls DI water	

C.) ICV / CCV: (True Value = 0.750 mg/l)
9.25 mls DI + 0.75 mls 10.0 ppm Reference Stock (purchased 10.0 ppm Ref. Stock).

D.) LCS / Matrix Spike: (True Value = 0.250 mg/l)
10.0 mls DI / sample + 0.250mls 10 ppm Standard Stock.

*** All standards, references, lcs and all dilutions are made only with bottled VWR DI!!!**

STANDARD OPERATING PROCEDURE

TOTAL SUSPENDED SOLIDS (TSS)

GEN 160.2

Revision 3
January 29, 2002

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed CONTROL
and the SOP still reflects current practice.
Initials: ______ Date: ___________
____
Initials: ______ Date: ___________

DOCUMENT

NUMBER:

Initials: ______ Date: __________ Initials: ______ Date: ______

1. **SCOPE**

1.1. Applicable Matrices - This method (EPA 160.2) is applicable to the measurement of total suspended solids in drinking, surface, and saline waters, domestic and industrial wastes.

1.2. Range of determination is 1 mg/L to 20,000 mg/L.

1.3. Practical Quantitation Limit (PQL) is 1 mg/L when 1000 mLs of sample are filtered.

2. **METHOD SUMMARY**

2.1. A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103-105°C. The increased weight of the filter represents the total suspended solids.

3. **DEFINITIONS**

3.1. **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.2. **Method Blank/ Prep Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank is carried through the entire analytical procedure.

3.3. **Laboratory Control Sample (LCS) –** A prepared standard is analyzed as a sample. Percent recoveries are calculated for the analyte detected.

3.4. **Batch –** a group of no more than 20 samples analyzed together

4. **INTERFERENCES**

4.1. Nonrepresentative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded if it is determined that their inclusion is not desired in the final result.

4.2. Excessive residue on the filter may form a water-entrapping crust. Limit the sample size to that yielding no more than 200 mg residue.

4.3. For samples high in total dissolved solids, thoroughly wash the filter to ensure removal of dissolved material.

4.4. Prolonged filtration times resulting from filter clogging may produce high results because of increased colloidal materials captured on the clogged filter.

4.5. Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because they can affect the results.

5. SAFETY

5.1. Wear gloves, lab coat and safety glasses when handling samples.

6. SAMPLE COLLECTION, CONTAINERS, AND STORAGE

6.1. Any type of container, glass or plastic, can be used.

6.2. Samples are nonpreserved and kept at 0-6°C until analysis to minimize decomposition of solids.

6.3. Holding time is 7 days. Holding time for work under ASP is 5 days from verified time of sample receipt.

6.4. Sample handling, storage, and custody procedures are discussed in SOP SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. Glass fiber filter discs, 4.7cm, Whatman GF/C

7.2. Filtration Apparatus

7.3. Aluminum Drying Dishes

7.4. Drying Oven

7.5. Desiccator

7.6. Analytical Balance, capable of weigh to 0.1 mg.

7.7. Forceps

7.8. Graduated Cylinder

8. PREVENTIVE MAINTENANCE

8.1. Replace desiccant in desiccators as needed. Desiccant may be dried and reused.

8.2. Check balance calibration prior to use. Keep balance clean and dry.

8.3. Add oil to the vacuum pump as needed.

9. REAGENTS

9.1. Kaolin powder – purchased commercially. Store at room temperature. Expires upon manufacturer's indications or three years from receipt, whichever is sooner.

9.2. Reference/LCS: To a tared plastic bottle, add 0.20 -0.30 g of Kaolin powder. Record actual weight used. Add DI water to 1000 g. The true value will be between 200 and 300 mg/L. Use as if it were a client sample. Store at 0-6 °C for up to one year.

9.3. MB – Use DI as if it were a client sample.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

11. PROCEDURE

11.1. Preparation of glass fiber filter disc:

Note: The filter should be handled with forceps at all times

Place the disc, wrinkle side up, on membrane filter apparatus. While vacuum is on, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings. Remove filter from the apparatus and place in a numbered aluminum dish. Dry the filters in an oven at 103-105°C for one hour. Remove to a desiccator and cool for at least 30 minutes.

11.2. Weighing of filters – Weigh the 1.0000 g "s" weight and record on tare sheet (attached). Transfer dish containing filter to the analytical balance and record the ID number. Weigh dish twice; successive weights must be within 0.5 mg of each other.

11.3. Selection of sample volume

11.3.1. The target residue on the filter is 10-200 mg. For clean samples, choose a sample volume up to 1000 mls. If during filtration of the initial volume, the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the sample volume should be decreased. A smaller sample volume may be used initially if it is visibly apparent that the residue on the filter will be higher than 200 mg. Use the entire 1000 mLs of sample if there is not much residue collecting on the filter.

11.4. Transfer the tared filter to the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to fit it to fritted support.

11.5. Shake the sample vigorously and transfer the predetermined sample volume selected to the filter using a graduated cylinder.

11.6. Filter the sample through the glass fiber filter. Record volume used on benchsheet (attached).

11.7. With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum for 3 minutes after all the water has passed through.

11.8. Carefully remove the filter and place into the aluminum dish. Dry at least one hour at 103-105°C. Cool in a desiccator and weigh.

11.9. Repeat the drying cycle until a constant weight is obtained (difference in weight should not be greater than 0.0005 g or 4% of previous weight). Record the second weighing on the bench sheet.

11.10. The temperature of the oven is recorded twice daily in a designated log book to maintain a compliant operating temperature. The time and temperature is also recorded in the "In/Out" log book whenever samples are put in or taken from the oven.

12. 0 QA/QC REQUIREMENTS

12.1. Run one duplicate per batch of ten samples. The DUP should have an RPD < 20%. If they do not, repeat the sample and duplicate or flag the associated sample results in the batch.

12.2. Run a Laboratory Control Sample per batch of 20 samples. The LCS recovery should be within the limits set in the Wetchem QC table in Appendix C of the Quality Assurance Manual. If it is not, determine the cause, fix the problem, and repeat the samples if volume and holding time permits. If not, flag the samples.

12.3. Analyze a Method Blank for every ten or fewer samples. The result of the blank must be less than the Reporting Limit. If it is not, determine the cause, beginning with visual inspection of the filter. If necessary, reanalyze the samples if volume and holding time permits, or flag the data.

13. DATA REDUCTION AND REPORTING

13.1. Calculation

$$mg\ total\ suspended\ solids\ /\ L\ =\ \frac{(A - B)\ x\ 1000{,}000}{sample\ volume,\ mL}$$

Where: A= weight of dried residue + dish (g)
B= weight of dish (g)

13.2. Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

Not available

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

Samples and sample residue may be washed down the drain. See SOP SMO-SPLDIS for further discussion on waste management.

16. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. *Method 2540D in Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.

18.2. *Method 160.2 EPA 600/4-79-020,* Revised March 1983.

19. **TRAINING OUTLINE**

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies in ADM-TRANDOC.

19.2. Observe Sample Preparation and Analysis. Follow Solids Analysis Training Plan Form.

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Perform an IDC (Initial Demonstration of Competency) by independently analyzing four mid-range standards prior to analyzing client samples. If recovery is within acceptable limits, complete Training Plan Form, summary spreadsheet and IDC certificate and file with QA. Continuing proficiency (CDC) will be demonstrated annually using a PE, a single blind, or a new 4 replicate study.

20. METHOD MODIFICATIONS

None

21. INSTRUMENT ADDENDUM

None.

22. ATTACHMENTS

Benchsheet
Tare sheet

23. CHANGES FROM PREVIOUS REVISION

23.1. Added Sections 14, 16, 17, and 20 for NELAC compliance
23.2. Added Batch to definitions
23.3. Added ASP holding time.
23.4. Added need to oil pump in Preventive Maintenance
23.5. Added MB to reagents
23.6. Added procedure for the weighing of samples in 11.2.
23.7. Changed MB frequency to ten samples instead of 20.
23.8. Eliminated statement concerning re-drying MB for corrective action and replaced with “determine the cause, beginning with visual inspection of the filter”
23.9. Eliminated statement concerning how to report TSS – this is done by LIMS.
23.10. Added Tare sheet to attachments

Columbia Analytical Services
1 Mustard St., Suite 250
Rochester, NY 14609

Total, Dissolved, or Suspended Solids

Analyst:________________ Date:__________ Time:_________ Pipet ID:__________

Total Solids _____ Method 160.3   Total Dissolved _____ Method 160.1   T. Suspended _____ Method 160.2

TS, TDS, TSS mg/L = $\frac{(A - B) * 1,000,000}{\text{Volume, mLs}}$ where: A = wgt (g) of dried residue + dish
B = wgt (g) of tared dish

Order Number	Client& Submission#	Dish I.D.	Sample Vol.(mLs)		Raw Data(g)
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	
				Gross1(A)	
				Gross2 (A)	
				Gross3 (A)	
				Tare (B)	
				Diff.	

Columbia Analytical Services
1 Mustard Street
Rochester, NY 14609

Tare Weights

Instument:_____Mettler AE240 Analytical Balance
_____Mettler AG204 Analytical Balance

Date: ____________
Analyst: ____________
Drying Tins ____________
Crucible 550 C ____________
Dish 180 C ____________
Dish 104 C ____________
Dish 550 C ____________
G/O Tins ____________

s Weight (s)____________________

ID Number	Weight	

ID Number	Weight	

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STANDARD OPERATING PROCEDURE

for

METALS DIGESTION,
SOILS, SEDIMENTS, AND SLUDGE FOR ICP ANALYSIS
FOR INDIANA PINES SITE

SOP No.: MET-3050pines

Revision: 0

September 28, 2004

Approved by: Christine Kutzer ______ 9/28/04
Supervisor — Date

Lisa Reyes ______ 9/28/04
QA Coordinator — Date

Michael K. Perry ______ 9/28/04
Laboratory Manager — Date

1 Mustard Street, Suite 250
Rochester, New York 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

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1 SCOPE AND APPLICABILITY

This SOP uses EPA SW-846 Method 3050B for the digestion of soils, sludges, or sediments for analysis by ICP. As stated in the EPA method, "this method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become environmentally available." By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment." This SOP was written specifically for the Indiana Pines Site.

2 SUMMARY OF METHOD

A representative aliquot of sample is digested in nitric acid and hydrogen peroxide. Hydrochloric acid is used as a final reflux acid.

3 DEFINITIONS

3.1 **Laboratory Duplicates** - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of duplicates indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 **Laboratory Control Sample Soil (LCSS)** - An aliquot of a soil to which known quantities of the method analytes are added. The LCSS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

3.3 **Matrix Spike** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The matrix spike is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.4 **Preparation Blank (PB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

3.5 **Digestion Batch** - A digestion batch is no more than 20 samples of the same matrix digested as a unit per day.

4 HEALTH AND SAFETY WARNINGS

Nitric and Hydrochloric acids are extremely corrosive. Care should be taken while working with these chemicals. Personal protective equipment including safety glasses (with side shields), gloves, and lab coat shall be worn when handling samples or reagents.

5 CAUTIONS

Antimony is easily lost by volatilization. Do not boil the digestate.

6 INTERFERENCES

Use more sample for those samples with high moisture content to meet detection limits.

7 PERSONNEL QUALIFICATIONS

At a minimum, personnel must have attained at least a 2-year degree in a science-related field and have successfully completed an Initial Demonstration of Capability and the Training Plan Form (attached). Training and Demonstration of Capability are in accordance with NELAC 2002 standard.

8 EQUIPMENT AND SUPPLIES

8.1 Eppendorf Pipettors
8.2 Funnels
8.3 Mortar and pestle
8.4 Tongue depressors
8.5 Filter paper
8.6 Hot Block Digestor with ETR-3200 Controller by Environmental Express, LTD.
8.7 Graduated block digestor cups
8.8 Block Digestor Filters.
8.9 CPI MOD Block Digestor

8.10 Reagent water - ASTM Type II deionized water.

8.11 Concentrated nitric acid (Baker Instra-Analyzed 69-70%): Store at room temperature in the dark in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.12 Concentrated hydrochloric acid (Baker Instra-Analyzed 36.5-38%): Store at room temperature in the original container or in glass. Expires per manufacturer's indications or one year from receipt if no indication is given.

8.13 Hydrogen peroxide (30%) - H_2O_2. Purchased commercially. Should be demonstrated to be free of impurities at levels which would interfere with sample determinations. Store at room temperature in the original container. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.14 ERA Soil Laboratory Control Sample (LCSS) - Concentrations and Performance Acceptance Limits distributed through vendor. Store at room temperature. Expires upon manufacturer's indications or 1 year from receipt if no indication is given.

8.15 Metals spiking solutions – Purchased commercially. See Table 1. Store at room temperature. Stocks expire upon manufacturer's indications or 1 year from receipt, whichever is sooner. Solutions prepared from stocks expire 6 months from preparation.

9 PROCEDURES

9.1 Sample Collection – Collect samples in purchased, certified clean glass or plastic.

9.2 Sample Handling and Preservation – Analyze samples within 6 months of sample collection. Store samples in a refrigerator or at room temperature. Sample receiving, handling, storage, and custody procedures are in accordance with NELAC 2002 Standard.

9.3 Sample Preparation

9.3.1 Set the temperature on the Block Digestor to a temperature that brings the sample temperature to 90-95°C without boiling.

9.3.2 The Hot Block is on a timer which can be set to turn on and off whenever necessary. To set timer press the timer button and choose the days M-F (Monday through Friday). Then choose the hour and minutes to start and stop the Block Digestor.

9.3.3 Label graduated hot block digestor sample cups with appropriate sample IDs for digestion.

9.3.4 Mix the sample thoroughly to achieve homogeneity using a tongue depressor or the mortar and pestle.

9.3.5 Weigh (to the nearest 0.01g) 1.00g to 1.50g of sample into labeled digestor sample cup. For sludges and sediments that have a high moisture content, use more sample. The goal is to use about 1g of dry weight sample. At this point add the appropriate spiking solutions (see Table 1) directly onto the designated spike sample prior to addition of reagents.

9.3.6 Unless otherwise specified by project requirements, the addition of acid should be as follows: Add 10ml of 1:1 HNO_3 and 1.5 mL of 1:1 HCl, cover with reflux cap and reflux for 15 minutes. The sample temperature should be 90-95°C. Allow the sample to cool, then add 5ml of concentrated HNO_3, cover and reflux for 30 minutes. Repeat the addition of 5ml of HNO_3 and reflux to 5 mLs. Do not allow the sample to go to dryness. CAUTION: Do not boil. Antimony is easily lost by volatilization.

9.3.7 Cool the sample and add 2ml of DI and 3ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessive effervescence. Heat until effervescence subsides and cool the sample cup.

9.3.8 If the effervescence does not subside, add 3 mLs of hydrogen peroxide with warming to each of the samples (including blanks and LCSs) in the batch. If necessary, continue to add 30% H_2O_2 in 1ml aliquots with warming until the effervescence is minimal, or until the general sample appearance is unchanged. Do not add more than 10ml of 30% H_2O_2.

9.3.9 Add 10 mL 1:1 HCL.

9.3.10 Cover and reflux the samples for 15 minutes without boiling. Allow to cool.

9.3.11 Rinse filters with 1:1 nitric acid and DI.

9.3.12 All samples are diluted to 100 mLs with DI. Quantitatively transfer the digestate to a graduated cylinder by pouring the sample through a prepared filter into the cylinder and rinsing the beaker and reflux cap with DI into the filter. Rinse the filter with DI. Bring to volume with DI. Pour into a labeled B-cup.

9.4 **Sample Analysis** – Give digested samples and a copy of the prep sheet to the ICP analyst. Analyze according to MET-6010Bpines.

9.5 **Troubleshooting -** All hoods in the Metals Prep Lab are wiped down once a week with DI water. The tops of all digestion hot plates are wiped down daily.

9.6 **Data Acquisition, Calculations and Data Reduction Requirements**

Digestion logs are used to record all sample volumes, spike volumes, etc. The Manufacturer's lot number for the reagents used are added to the digestion log (see attached digestion log benchsheet).

10 DATA AND RECORDS MANAGEMENT

10.1 Responsibilities - It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. Final review and sign-off of the data is performed by the department supervisor or designee.

10.2 Data will be reviewed after ICP analysis according to MET-6010Bpines.

11 QA/QC REQUIREMENTS

11.1 Each day, digest one laboratory control sample (LCS) per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use the appropriate solid laboratory control sample (LCSS) for soils analysis.

11.2 Each day, digest one blank per digestion batch, or per 20 samples, or per EPA SDG group, whichever is more frequent. Use D.I. water and follow the digestion procedures.

11.3 Each day, prepare one duplicate and one spiked sample with each digestion batch, or per twenty samples, or per EPA SDG group, whichever is more frequent. At times, specific samples will be assigned as duplicates of spikes depending on client requirements.

11.4 Matrix spikes are prepared by adding the appropriate volume of spiking solution (See Table 1).

11.5 See MET-6010Bpines for applicable QC limits and corrective action.

12 REFERENCES

"Test Methods For Evaluating Solid Waste, Physical/Chemical Methods". EPA SW846, Third Edition, December 1996.

NELAC, 2002 Standard.

Table 1 Spiking Concentrations for LCS and MS Samples

SPIKE SOLUTION A		1.00ml Spk A	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
AL	200	**NI**	50
AS	4	**SE**	1
BA	200	**AG**	5
BE	5	**TL**	200
CD	5	**V**	50
CR	20	**ZN**	50
CO	50	**B**	100
CU	25	**CA**	200
FE	100	**MG**	200
PB	50	**NA**	2000
MN	50	**K**	2000

SPIKE SOLUTION B		1.00ml Spk B	to Final Vol of 100ml
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
SB	50	**TI**	50
MO	50	-	-

INDIVIDUAL METALS	0.10ml Spk. to Final Volume of 100ml	**INDIVIDUAL METALS**	0.5ml Spk. to Final Volume of 100ml
Metal	***Conc. (ug/mL)***	***Metal***	***Conc. (ug/mL)***
SE	1000	**SN**	1000

CAS-Rochester ICP Soil Digestion Log

6010B/846 // 200.7/136 // ASP/CLP4.1

Batch ID:

Analyst: ____________ Date: ________

Spike Witness / Lot Approval: ____________

Batch Temp:

Prep Method: SW846 3050 // CLP

Digest: Initial // Redigest of: ____________

Report Type: Routine // ASP // Pkg5

	Submission / Order #	Initial Wgt. (g)	Final Vol (ml)	Initial Color / Texture	Final Color / Clarity	Metals	Spike Vol (ml)
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

Spiking Standards / Reagent Lot #:

Spike A,B: ________ Spike #4: ________
TCLP Spk: ________ TCLP Ba: ________
Se Std: ________ Sn Std: ________
HNO3: ________ HCL: ________
H2O2: ________ LCSS: ________

Color / Clarity Key:

Color: **C** = Colorless ; **Y** = Yellow ; **B** = Brown
BL = Black ; **G** = Grey ; **W** = White
Clarity: **CDY** = Cloudy ; **CLR** = Clear ; **OP** = Opaque
Texture: **F** = Fine ; **M** = Medium ; **CS** = Coarse ; **NAQ** = Non Aqueous

01

Comments: ____________

STANDARD OPERATING PROCEDURE

TOTAL ORGANIC CARBON or TOTAL INORGANIC CARBON IN SOILS

GEN-TOCLK/9060/TICLK

Revision 2

January 17, 2005

Approved By: ______________________________ ___________
Supervisor Date

______________________________ ___________
QA Coordinator Date

______________________________ ___________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: __________

1. SCOPE AND APPLICATION

1.1. This procedure is applicable to the determination of Total Organic Carbon (TOC) in soils and sludges using the EPA document "Determination of Total Organic Carbon in Sediment" prepared by Lloyd Kahn (EPA 1988) or EPA SW846 9060. Total Inorganic Carbon (TIC) may be calculated by subtraction of TOC from Total Carbon(TC).

1.2. The current system will measure up to about 1500 ug/g C when the smallest sample volume is used. When a range extender is used on the instrument, the range is extended to about 8000 ug/g C.

1.3. Normal operating parameters yield a Practical Quantitation Limit (PQL) of 300 mg/Kg. Equivalent nomenclature for PQL includes Estimated Quantitation Limit (EQL) and Method Reporting Limit (MRL).

1.4. Data are reported in mg/kg on a dry weight basis.

2. METHOD SUMMARY

2.1. Treatment prior to analysis of carbon

2.1.1. For TOC - Inorganic Carbon from carbonates and bicarbonates is removed by treatment with acid.

2.1.2. For TC - Inorganic Carbon from carbonates and bicarbonates is NOT removed by treatment with acid.

2.1.3. For TIC - The samples are put through the process twice – once to measure Total Carbon (TC), and once to measure Total Organic Carbon (TOC). The Total Inorganic Carbon (TIC) is calculated by difference.

2.2. The carbon compounds are decomposed into carbon dioxide and other gases by pyrolysis at 800 °C in the presence of air. The interfering gases are removed by a sparger/scrubber system. The carbon dioxide that is formed is determined by direct nondispersive infrared detection that has been calibrated to directly display the mass of carbon dioxide detected. The resulting carbon mass in the form of carbon dioxide is the equivalent to the mass of carbon (TOC or TC) originally in the sample.

3. DEFINITIONS

3.1. **Initial Calibration -** analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the system.

3.2. **QA/QC Samples**: Samples added to a sample preparation batch, or an analytical batch to provide quality assurance checks on the analysis.

3.2.1. **Matrix Spike (MS**) - In the matrix spike analysis, a predetermined quantity of standard solution is added to a sample matrix prior to sample analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the methods used for the analyses. Percent recoveries are calculated for the analyte detected.

3.2.2. **Duplicate Sample (DUP**) - A laboratory duplicate. The duplicate sample is a separate field sample aliquot that is processed in an identical manner as the sample proper. The relative percent difference between the samples is calculated and used to assess analytical precision.

3.2.3. **Laboratory Control Standard (LCS) -** In the LCS or blank spike analysis, predetermined quantities of standard solutions of certain analytes are added to a blank prior to sample analysis. Percent recoveries are calculated for the analyte detected and used to verify the linear range daily.

3.3. **Relative Percent Difference (RPD) –** The absolute value of the difference of two values divided by the average of the same two values. Used to compare the precision of the analysis. The result is always a positive number.

3.4. Batch - Samples processed together as a unit, not to exceed 20 investigative samples. See ADM-BATCH for further discussion.

3.5. **Independent Calibration Verification (ICV)** - ICV solutions are made from a stock solution which is different from the stock used to prepare calibration standards and is used to verify the validity of the standardization.

3.6. **Continuing Calibration Verification Standard (CCV)** - A reference analyzed daily at specified intervals and used to verify the ongoing validity of the instrument calibration.

3.7. **Instrument Blank (ICB/CCB)** - The instrument blank (also called initial or continuing calibration blank) is a volume of blank reagent of composition identical to the samples (DI in this test). The purpose of the CCB is to determine the levels of contamination associated with the instrumental analysis.

3.8. **Method Detection Limit (MDL):** a statistically derived value representing the lowest level of target analyte that may be measured by the instrument with 99% confidence that the value is greater than zero

3.9. **Method Reporting Limit (MRL):** The minimum amount of a target analyte that can be measured and reported quantitatively. The MRL is equivalent to Practical Quantitation Level (PQL) and Estimated Quantitation Level (EQL). Typically, the MRL is calculated as five times the MDL (although this is a rule of thumb and not intended to be a strict policy of establishing the MRL for a compound).

4. INTERFERENCES

Volatile organics in sediments may be lost in the decarbonation step resulting in low bias. Minimize loss of organic compounds by bacterial decomposition and/or volatilization by maintaining the sample at 0-6 °C.

Contamination by carryover can occur when high level samples immediately precede samples containing significantly lower levels of contamination. Pay close attention to samples which follow high level samples. Re-analyze if contamination is suspected.

5. SAFETY

- All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

- Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

- Nitric Acid is used in this method. This acid is extremely corrosive and care must be taken while handling it. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

- The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. Sources of flammable gases (e.g., pressurized hydrogen) should be clearly labeled.

- Refer to the Safety Manual for further discussion of general safety procedures and information. Always wear chemical eye, skin, and clothes protection when handling samples or working with reagents.

6. SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

6.1. Samples are collected in purchased certified clean containers free of organic contaminants. Glass is preferable.

6.2. Because of the possibility of oxidation or bacterial decomposition of certain components, the samples should be kept cool (0-6°C) and protected from sunlight and atmospheric oxygen from time of collection to analysis. Holding time for samples is 14 days.

6.3. Further sample handling, storage, and custody procedures are discussed in SMO-GEN.

7. APPARATUS AND EQUIPMENT

7.1. Model DC-190 Total Organic Carbon Analyzer with Boat Module. (Dohrmann)

7.2. Combustion boat: Platinum.

7.3. The linear range extender (Dohrmann part # 885-462) is used for high level samples. It consists of an expansion chamber attached to the 200 ml/min air line from the furnace/sparger and to a 400 ml/min line of air that acts to dilute the CO_2 gas in the standards and samples by a factor of 1/3.

7.4. Volumetric pipets/glassware and/or adjustable micro-pipets.

7.5. Printer

7.6. Drying oven capable of maintaining 70 ± 2 °C.

7.7. Drying tins

7.8. Small glass test tubes

8. PREVENTIVE MAINTENANCE

8.1. For the most reliable performance of the instrument, the following schedule of routine maintenance is suggested:

8.1.1. Daily:

- Condition the boat: Place fresh quartz wool plug and a few drops of HNO_3 in the Pt boat. All boats should be "conditioned" prior to any runs in order to remove any CO_2 that may have built up on the boat overnight. Place the boat in the hatch. Close the hatch (the sparger will bubble if the hatch is closed properly. Always watch for this every time the hatch is closed.) Advance the Pt Boat into the furnace. Allow it to bake for ~2-3 minutes, so that any carbonaceous material on the boat is removed. Retract the Pt Boat into the hatch block, allow to cool at least 30 seconds. Do this for all boats.

- Check the Cu/Sn scrubber. If dissolved or clogged, replace with fresh Cu and/or Sn.

8.1.2. Weekly:

- Check gas cylinder – replace when necessary
- Adjust IR "zero" if necessary
- Leak check the carrier gases
- Replace the sparger DI with UPDI acidified with phosphoric acid to pH <2

8.1.3. Every 2 Weeks or Earlier:

Check the Boat Module's combustion tube. Replace the cobalt oxide catalyst if necessary. If the combustion tube becomes etched/"cloudy" looking, consider replacing it. The etching is produced by interfering gases in samples, and can cause a "slowdown" of movement of the carrier gas through the tube, resulting in "time out errors" during detection.

8.2. Maintenance log - All Preventive maintenance, as well as instrument repair, should be documented in the appropriate instrument maintenance log. Most routine maintenance and troubleshooting are performed by CAS staff. Other maintenance or repairs may, or may not require factory service, depending upon the nature of the task. Any maintenance performed by outside services must also be documented – either through notes in the log or through documents provided by the service. The log entries will include the date maintenance was performed, symptoms of the problem, serial numbers of major equipment upgrades or replacements. The datafile name of the first acceptable run after maintenance is to be documented in the maintenance log.

9. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1. Reagent (laboratory deionized) water. If DI appears to be a source of contamination, use DI that has been run through the Millipore system in the VOA lab. It is suggested to occasionally make reagents with this Millipore water and analyze the tap DI at the low level to determine if it has a value above 0.1 mg/L.

9.2. Phosphoric Acid: reagent grade, purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.3. Cobalt oxide catalyst: Place about 2 inches of cobalt oxide in the combustion tube with both ends bound by a tuft of quartz wool. Condition fresh cobalt oxide by placing a piece of tubing from the exit of the tube in dilute NaOH for at lease 1 hour with the air and furnace on.

9.4. Nitric Acid, concentrated: Purchased commercially. Store at room temperature. Expires upon manufacturer's indications or 3 years from receipt if no other indication is given.

9.5. 1+1 Nitric Acid (HNO_3): Add a volume of DI to an equal volume of concentrated nitric acid. Store at room temperature. Expires in one year.

9.6. Sparger solution: Fill the sparger with UPDI from a squirt bottle. Acidify the water with a couple drops of concentrated phosphoric acid to pH 2.

9.7. Gas Service: Compressed Air.

9.8. **<u>Standards Preparation General Information and Disclaimers</u>**

All of the preparation instructions are general guidelines. Other technical recipes may be used to achieve the same results. Example – a 20 ppb standard may be made by adding 1 uL of 200 ppb to 10 mLs or may be made by adding 4 uL of 50 ppb to 10 mLs. The preparation depends upon the final volume needed and the initial concentration of the stock. Reasonable dilution technique is used.

The initial calibration curves given are typical, but also subject to variation due to detection levels needed. The lowest concentration level shall be at the method reporting level. The remaining levels should define the working linear range of the analytical system.

All Standards must be traceable using the CAS lot system (ADM-DATANTRY).

9.9. Organic Carbon stock solutions:

9.9.1. Standard Stock Solution (10,000 ppm C): Stock solution is prepared by adding 10.64 g of Potassium Biphthalate (KHP) (previously dried to a constant weight at 104°C) into a 500 mL volumetric flask. Dilute to volume with reagent water. Store in amber glass at room temperature for up to 1 year.

9.9.2. Reference Stock Solution (10,000 ppm C): Stock solution is prepared by adding 10.64 g of KHP (previously dried to a constant weight at 104°C and from a different manufacturer) into a 500 mL volumetric flask. Dilute to volume with reagent water. Store in amber glass at room temperature for up to 1 year.

9.10. Inorganic Carbon Stock Solution (10,000 mg/L inorganic C): Stock solution is prepared by adding 8.824 g of Sodium Carbonate (previously dried to a constant weight at 104°C and from a different manufacturer) into a 100 mL volumetric flask. Dilute to volume with reagent water. Store in amber glass at room temperature for up to 1 year.

9.11. ICV/CCV: Add 50 uL of 10,000 mg/L Reference Stock to 100 mg of Ottawa Sand. True Value = 5000 ug/g.

9.12. LCS for TC or TOC: Add 20 uL of 10,000 mg/L Standard Stock to 100 mg of Ottawa Sand. True Value = 2000 ug/g

9.13. LCS for TIC – Add 20 uL of 10,000 mg/L Inorganic Carbon Stock to 100 mg of Ottawa Sand. True Value = 2000 ug/g.

9.14. Matrix Spikes: Add 20 uL of 10,000 mg/L Standard Stock to a similar mass of sample which was used for the sample analysis. TV = 2000 ug/g when 100 mg of sample is used. Prepare fresh before use.

9.15. Calibration Standards

***Note: When using an adjustable pipet, record the pipet ID of the pipet used.

9.15.1. Prepare Single Point Calibration Standard by adding 50 uL of 10,000 mg/L Organic Standard Stock to 100 mg Ottawa Sand.

9.15.2. Prepare a 1000 ppm working stock for the less concentrated check standards – Dilute 1.0 mL of 10,000 ppm Standard Stock to 10 mLs with reagent water. Prepare fresh before use.

9.15.3. Prepare curve check standards as follows:

uL 10,000 ppm Standard Stock	Weight (mg)	Final Conc. (ug/g)
80	100	8000
50	100	5000
30	100	3000
100 uL 1000 ppm working stock	100	1000
50 uL 1000 ppm working stock	100	500
30 uL 1000 ppm working stock	100	300

** Note – These (above) curve check standards are to verify the instrument response only. They are not used to calculate sample results

10. RESPONSIBILITIES

It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

11. PROCEDURE

11.1. Be sure the analyst has a current Demonstration of Capability and the system has a current MDL.

11.2. Turn on the air gas flow and confirm 30 psi delivery pressure. Maintain this delivery pressure.

11.3. **Initial Power Up**:

11.3.1. Turn on:

- The 70 °C oven
- The Boat Module Furnace
- The DC-190 Furnace and Carrier Gas. Confirm 200 mL/min readout. Even though soils and the Boat Module do not need the DC-190

Furnace and carrier gas on, the instrument software does.

- Allow time for all to come to correct temperature. The LED's for each will turn from red to green when ready.

11.3.2. Confirm that the desired analysis mode is properly selected. The TC and BOAT LED's on the DC-190 should be lit.

11.3.3. Condition the boat.

11.4. Initial Calibration

11.4.1. Prior to calibrating, reset the software to original conditions by pressing "Calibrate", 7, 1. Press "Yes" when prompted. This will reset the calibration factor to 1.0. Be sure to then make sure that the sample size (50 uL) and concentration (10,000) of the calibration stock standard are entered correctly before starting a new calibration. Press "Boat" then "1" to change ug/g to mg/L. Press "3" to print.

11.4.2. Standard Analysis - A single point calibration technique is used because the infrared detector response has been linearized. It is then verified with the other standards. The single-point calibration standard is run in duplicate, at least.

11.4.2.1. Weigh 100 mg of Ottawa Sand into the Pt Boat.

11.4.2.2. Add 1+1 HNO_3 dropwise until no effervescence is visible.

11.4.2.3. Place the boat in the oven at 70-75 °C for 10-15 minutes.

11.4.2.4. Remove the boat from the oven, place it in the hatch. Add 50 uL of the 10,000 mg/L Standard Stock to the PT Boat. Close the hatch (the sparger will bubble if the hatch is closed properly. Always watch for this every time the hatch is closed.)

11.4.2.5. Press the START button on the DC-190. Enter the "sample ID." The "Wait" LED will light momentarily while the instrument checks the baseline.

11.4.2.6. When the "Inject" LED lights, advance the boat into the furnace at the rate of about 2 inches per second.

11.4.2.7. The "Acquire" light will turn on. The analysis will take about 6-8 minutes to finish, at which point the printer will print out the result, and the screen will ask "Continue Y/N?" Press the "Yes" button to do another.

11.4.2.8. Repeat the Standard Analysis steps for the replicate standard. If a third replicate is desired, press "Yes" at the end of the analysis. (If an outlier needs to be removed from the calibration, see page 6-26 of the DC-190 Ops Manual. At least 2 replicates must be run for the initial calibration.) Press “No” to end the initial calibration.

11.4.3. Software Calibration

11.4.3.1. Press “Calibrate” to review the calibration menu. Verify that the sample size and standard concentration are correct.

11.4.3.2. Press “5” to update the Calibration Factor. This will be calculated, displayed on the menu, and printed out.

11.4.4. If necessary, set instrument blank - Perform the standard analysis steps except adding 50 uL of UPDI instead of standard. After 2 replicates of the blank, press “No”, “Calibrate” and “6” to update the system blank.

11.4.5. Change the concentration units from mg/L to ug/g by pressing “Boat” then “1”.

11.5. Run the curve check standards to verify linear range. The instrument calculated results of the curve check standards should be within 10% of the true value and 20% for the lowest curve check standard. If they are not, repeat the calibration

11.6. Run the ICV, ICB, and a LCS to verify the curve.

11.7. **Daily Sample Analysis and Continuing Calibration Verification**

The calibration is confirmed with every run by the CCV, CCB, and LCS. Daily, every run is started with a CCV, CCB, and LCS and is closed with a CCV, CCB, as well as a CCV/CCB set every 10 samples and an LCS every 20. The instrument only needs to be recalibrated when these QC become unacceptable, or at least once a year.

11.7.1. Complete the initial power up steps

11.7.2. Condition Pt boat.

11.7.3. Sample preparation

11.7.3.1. Thoroughly mix sample and place a small aliquot (~2 g) in a drying tin.

11.7.3.2. Allow to dry overnight in a hood at room temperature.

11.7.3.3. Grind the sample with the bottom of a small glass test tube to break up aggregates.

11.7.3.4. Discard rocks.

11.7.3.5. Weigh 100 mg (or less depending on anticipated concentration) of sample or Ottawa Sand into the Pt Boat.

11.7.3.6. For TOC - Add 1+1 HNO_3 dropwise until no effervescence is visible. For TIC, separate aliquots of the sample will be analyzed – one with the acid added (TOC) and one with no acid added (TC). TIC will be the difference between the two results.

11.7.3.7. If acid has been added, place the boat in the oven at 70-75 °C for 10-15 minutes. Remove the boat from the oven.

11.7.4. Sample analysis

11.7.4.1. Spike at this time if needed.

11.7.4.2. The system is set up using the "Range Extender". This setup creates back-pressure. The release of pressure when the sample hatch is opened can cause the carrier gas to back-flow through the mist-trap and into the sparger, thus forcing the sparge liquid into the combustion tube/cobalt oxide. To prevent this, the following procedure should be followed:

11.7.4.2.1. **Before Opening the Hatch**: remove one end of the line from the sparger to the mist-trap.

11.7.4.2.2. Open the hatch and insert the boat. Close the hatch.

11.7.4.2.3. **After Closing the Hatch**: replace the end of the line from the sparger to the mist-trap. The sparger will bubble if the hatch is closed properly. Always watch for this every time the hatch is closed.

11.7.4.3. Press the START button on the DC-190. Enter the "sample ID" and the mg of sample. The "Wait" LED will light momentarily while the instrument checks the baseline.

11.7.4.4. When the "Inject" LED lights, advance the boat into the furnace at the rate of about 2 inches per second.

11.7.4.5. The "Acquire" light will turn on. The analysis will take about 6-8 minutes to finish, at which point the printer will print out the result, and the screen will ask "Continue Y/N?" Press the "No" button to analyze another sample.

11.7.4.6. Samples analyzed by 9060 are to be analyzed in quadruplicate. Lloyd Kahn samples are analyzed only once. Samples for TIC are analyzed once for TOC (with acid) and once for TC (without acid).

12. QA/QC REQUIREMENTS

12.1. QC Samples and Acceptance Criteria

12.1.1. LCS for TOC - An LCS must be analyzed with each batch of 20 or fewer samples. Results must be within the limits in Appendix C of the Quality Assurance Manual.

12.1.2. LCS for TIC - Analyze the inorganic carbon LCS per batch. Results should be within 75-125% of the true value until enough points are available that calculated limits may be established.

12.1.3. A CCV must be analyzed following every tenth injection and at the end of the run. Recovery must be within 15% of the value (85-115%).

12.1.4. A CCB must be analyzed following every CCV. The result must be below the PQL.

12.1.5. Duplicates- One sample per 20 samples, must be analyzed in duplicate. If one or both of sample or duplicate is < 5X RL, the control limit is ± RL.

12.1.6. Matrix Spikes- One spike sample must be analyzed per 20 samples. The matrix spike recovery must within the limits in Appendix C of the Quality Assurance Manual.

12.1.7. Matrix Spike Duplicates – One sample for every 10 samples must be spiked and analyzed in duplicate for 9060. The % recovery limits and corrective action are the same as the matrix spike and the RPD limits and corrective action are the same as the duplicate.

12.2. Corrective Action

12.2.1. CCV, CCB, LCS

12.2.1.1. Check for gas leaks, sufficient reagent, and other instrument problems.
12.2.1.2. Remake working standard and reanalyze.
12.2.1.3. Recalibrate if QC is still out of control.
12.2.1.4. When instrument is back in control, reanalyze samples bound by out of control QC.

12.2.2. Duplicates

12.2.2.1. Check for gas leaks, sufficient reagent, and other instrument problems.
12.2.2.2. If the RPD value between sample results above 5X RL exceed 30% reanalyze the pair or flag the associated data.

12.2.3. Matrix spike

12.2.3.1. Check for gas leaks, sufficient reagent, and other instrument problems

12.2.3.2. If there are no such problems and recovery of the MS fails on a sample, the batch is considered acceptable as long as the LCS meets acceptance criteria. It is recommended that the MS/MSD be reprepared and reanalyzed to confirm the outliers, however it is not required due to probable matrix interferences.

13. DATA REDUCTION AND REPORTING

13.1. Calculations used by the DC-190 system

13.1.1. The equations used internally for determining a calibrated result:

$$Y = (Fx - b)/V$$

Where:
- Y = Concentration (calibrated) of sample
- x = Peak with background subtracted. Normally invisible to the user. The displayed value, y, may be made to equal x by setting F,b, and V to the appropriate values (1, 0, and 1, respectively)
- F = "Calibration Factor". This is the slope of the linear fit line.
- b = Intercept. This is an internal parameter which is invisible to the user.
- SB = "System" Blank = b/V
- V = Sample volume (or mass)

The quantities F and SB are the ones displayed on the calibration menu and are the ones which can be edited directly.

13.1.2. The Calibration Factor and Blank are calculated by:

$$F_n = F_o(C_s/Y_s)$$
$$b_n = b_o(F_n/F_o)$$

Where:
- C_s = Concentration of the standard
- o = Old value
- n = New value
- s = Value of the standard

Both F_n and b_n are re-calculated each time either the Calibration Factor or the System Blank are updated. It should be noted that if the old value b_o is already 0, the new value b_n and therefore SB will also be 0. This provides a means to have the system effectively do a one point calibration update when it calculates a new Calibration Factor. These equations may also be used to manually calculate the values and enter them on the "Calibration" menu directly.

13.2. The instrument calculates the ug/g C in the sample from the linearized response and the sample volume using the above equations. As long as the user enters the calibration correctly and the sample volume correctly, the instrument will print the final result with no further manipulation.

13.3. The result from the instrument is a dry weight result and is not to be further adjusted in LIMS.

13.4. Data must be reviewed by the analyst and a peer (supervisor or qualified analyst) using a Data Quality Checklist before the results are validated and reported to the client. Further data review policies and procedures are discussed in ADM-DREV.

14. METHOD PERFORMANCE

Reporting limits are based upon an MDL study performed according to ADM-MDL and filed in the MDL binders in the QA office.

Demonstration of Capability is performed upon instrument set-up , whenever a new analyst begins independent analysis, and annually thereafter according to ADM-TRANDOC and section 19 below. The documentation of this method performance is retained by the Quality Assurance office

15. WASTE MANAGEMENT AND POLLUTION PREVENTION

- It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

- The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

- Excess, unused sample and testing byproducts are disposed following the procedures in SMO- SPLDIS.

16. CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

If data is produced that is out of control, the samples are to be re-analyzed with in-control QA whenever possible. See corrective actions in Section 12 of this SOP and in the applicable Figures in Section 12 of the Quality Assurance Manual.

17. CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE

DATA

If data is produced that is out of control and is not to be re-analyzed due to sample volume restrictions, holding times, or QC controls can not be met, follow the procedures in Section 15 of the Quality Assurance Manual.

18. REFERENCES

18.1. "Total Organic Carbon in Soils" Lloyd Kahn EPA 1988.

18.2. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, USEPA SW-846.

18.3. OI Analytical, *Model 1010 Wet Oxidation TOC Analyzer Operator's Manual*, Revision 9.1, June 2001

19. TRAINING OUTLINE

19.1. Read current SOP and applicable methodologies. Demonstrate a general understanding of the methodology and chemistry. Follow policies and procedures in ADM-TRANDOC.

19.2. Observe Sample Preparation and Analysis, including instrument operation and maintenance. Follow Training Plan Form.

19.3. Participate in the methodology, documentation, and data reduction with guidance.

19.4. Demonstrate Competency by performing the analysis independently. Analyze a known proficiency or standard four times for Initial Demonstration of Capability. If recovery is within acceptable limits, complete training plan form and IDC certificate. Turn paperwork in to QA for acceptance and filing.

19.5. Continuing Demonstration of Capability will be performed annually using an internal unknown, a PE, or a new four replicate study.

20. METHOD MODIFICATIONS

Method 9060 is for waters and wastes but is useful for soils as described here.

21. INSTRUMENT-SPECIFIC ADDENDUM

The instrument manual is located next to the instrument. Refer to this manual for instrument setting or specifications not described in this SOP.

22. ATTACHMENTS

Benchsheet

23. CHANGES FROM PREVIOUS REVISION

- Eliminated most wording about High Level vs. Low Level since the range extender is always used at this time.
- Added TIC throughout
- Changed references to TOC to Carbon, where applicable, to be inclusive for the addition of TIC to this SOP
- 2.1 – Added section about pre-treatment of sample
- 4 – Added to be cautious of contamination by carry-over
- 5 – Changed wording of Safety section for consistency with other SOPs
- 8 – Expanded upon wording of Maintenance Log
- 9 – Rearranged to put Reagents together and Standards together
- 9- Eliminated 100 ug/g standard
- 9 – Added Standards Prep General Info and Disclaimers
- 12 – Modified wording of corrective actions for consistency
- 14 – Added ADM-Trandoc for consistency with other SOPs
- 15 – Modified for consistency with other SOPs
- 18 – Added reference to TOC Analyzer Manual (used to verify method for TIC)

COLUMBIA ANALYTICAL SERVICES
1 Mustard St., Rochester, NY

TOC SOILS ANALYSIS
by L. Kahn Method (EPA 1988) or EPA 9060

Analyst: ____________________ Date: ____________________

Pipet ID: ____________________ Start Time: ______________

Curve Date:

Corr. Coeff.:

Position #	Sub. #	Order #	Sample Amt. (mg)	Result (ug/g)	Baseline Before Inject	Baseline After Inject
1	Std: 50 uL of 10,000 ppm Std		Calibration	Source:		
2	Std: 50 uL of 10,000 ppm Std		Calibration	Source:		
3	ICV: True Value = 5000		100			
4	ICB: 50 uL of UPDI		100			
5	LCS: True Value = 2000		100			
6	8000	Curve Check	100			
7	5000	Curve Check	100			
8	3000	Curve Check	100			
9	1000	Curve Check	100			
10	500	Curve Check	100			
11	300	Curve Check	100			
12	ERA CHECK	TV = 12700	9.9			
1	CCV					
2	CCB					
3	LCS					
4						
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"Time Out Error": Baseline did not return after ignition to within 0.250 mV of the pre-ignition baseline

p:\l\1\g\forms\bnchsht\toc-s-lk.xls Cal Curve

COLUMBIA ANALYTICAL SERVICES
1 Mustard St., Rochester, NY

TIC SOILS ANALYSIS
by Modified L. Kahn Method (EPA 1988) or EPA 9060

Analyst: ____________________ Date: ____________________

Pipet ID: ____________________ Start Time: ______________

Curve Date: 6/15/04

Corr. Coeff.: 0.99974

Position #	Sub. #	Order #	Sample Amt. (mg)	Without acid TC Result (ug/g)	With acid TOC Result (ug/g)	(TC - TOC) TIC Result (ug/g)
1	Std: 50 uL of 10,000 ppm Std.		Calibration	Source: TOC1-123A		
2	Std: 50 uL of 10,000 ppm Std.		Calibration	Source: TOC1-123A		
3	ICV	TV=5000	100	4916		98.3%
4	ICB		100	40.39		
5	LCS	TV=2000	100	1861		93.1%
6	8000	Curve Check	100	7761		97.0%
7	5000	Curve Check	100	5267		105%
8	3000	Curve Check	100	3187		106%
9	1000	Curve Check	100	933.1		93.3%
10	500	Curve Check	100	499.8		100%
11	300	Curve Check	100	254.6		84.9%
12	ERA CHECK	TV=12700	100	14160		111%
1	CCV	TV=5000	100			
2	CCB		100			
3	OrgC LCS	TV=2000	100			
4	InOrgC LCS	TV=2000	100			
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"Time Out Error": Baseline did not return after ignition to within 0.250 mV of the pre-ignition baseline

STANDARD OPERATING PROCEDURE

for

The Determination of Method Detection Limits

SOP Code: ADM - MDL

Revision: 5

August 1, 2003

Approved by: Lawrence J Jacobs _______________ 8/1/2003
Quality Assurance Director — Date

_______________ 8/1/03
Chief Quality Officer — Date

Steve Vincent _______________ 8/1/2003
President — Date

1317 South 13th Avenue
Kelso, Washington 98626

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ____________________

Initials: ______ Date: ____________

Standard Operating Procedure for The Determination of Method Detection Limits

1.0 PURPOSE

This standard operating procedure (SOP) documents the procedure for the determination of method detection limits (MDLs).

2.0 APPLICABILITY

The procedure described in this SOP is designed for applicability to a wide variety of sample types ranging from reagent (blank) water or wastewater containing the analyte to solids (such as soil) containing the analyte to the analyte in a gaseous matrix. The MDL for an analytical procedure will vary as a function of sample matrix. This SOP requires a complete, specific, and well-defined analytical procedure. It is essential that all sample-processing steps of the analytical procedure are included in the deter-mination of the MDL; that is, all the steps that a sample is processed through, from sample preparation to analytical completion, must be included in the MDL determination. The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample. This SOP for the determination of MDLs was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device or instrument-type independent.

3.0 DEFINITIONS

3.1 Method Detection Limit (MDL)

The MDL is the minimum concentration of a substance or analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte.

3.1.1 The Calculated MDL (MDL_C) is the MDL as calculated in Section 6.10 and will typically contain two or more significant figures.

3.1.2 The Reported MDL (MDL_R) is the MDL that is used for reporting purposes. MDLs for <u>organic analytes</u> will be reported with two significant figures.[1] MDLs for <u>inorganic analytes</u> will be reported with either one or two significant figures depending upon the number of significant figures in the analytes' MRL.[2]

3.2 Analytical Procedure

The written, step-by-step description of the operation by which samples are processed in order to obtain the concentration of an analyte in a sample.

[1] Organic analyte MDLs: see Section 6.3.2 in Reference 9.2.
[2] Inorganic analyte MDLs: see Section 6.4.2 in Reference 9.2

3.3 Spike Level

The spike level is the known concentration of analyte that is added to a matrix for the determination of the MDL.

3.4 Interferences

Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of known or unknown species (interferent) that hinder an accurate analysis of the target analyte(s).

3.5 Matrix[3]

3.5.1 When the matrix analyzed is aqueous (includes ground water, surface water, waste water, drinking water, etc.), analyte-free reagent water is to be used. When the matrix analyzed is solid (includes soil, sand, tissue, or other solid materials), analyte-free soil, sand, tissue, or a suitable material is to be used. When the matrix analyzed is gaseous (i.e., air or emissions), an analyte-free, inert gas (such as zero-grade air or ultrapure helium or nitrogen) is to be used.

3.5.2 If the analysis is performed on a matrix for which there is not available an appropriate or similar, analyte-free matrix (such as, metals analysis on soil samples), the MDL analysis will be done as prescribed by the SOP for the analysis except the sample (weight) will be omitted; that is, the analysis will be done on all the reagents but without addition of any sample.

4.0 DISCUSSION

The MDL is a property of the analytical procedure, sample matrix, and measurement system (e.g., an instrument if one is used in the analytical procedure). The MDL is a statistic. It is an estimate that includes both the systematic and random errors that are an inherent part of the analytical procedure. The MDL for a given analyte will be unique for the sample's matrix and may be different than the MDLs shown in published methods. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

The relative uncertainty of an analytical measurement increases as the measured value approaches the MDL and at the MDL the uncertainty in the measured value may be 100% or greater.

[3] For a list of matrices, see Section 3.3 in Reference 9.3

Regarding Method Proficiency, in Chapter One of the Third Edition of SW-846 (as updated) it states:

> *Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit (MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.*

This SOP is based upon the procedure described in *40 CFR Part 136*, *Appendix B* (Reference 9.1).

5.0 RESPONSIBILITIES

It is the responsibility of the laboratory manager, working with the quality assurance program manager (QA PM) and department managers and supervisors, to schedule MDL determinations as they come due. It is the responsibility of the QA PM to track the status of MDLs. Completed MDL determinations are to be reviewed by the QA PM and approved by the laboratory manager and/or the QA PM before they are implemented. The QA PM is responsible for maintaining the MDL file described in Section 8.0.

6.0 PROCEDURE

6.1 General Requirements

6.1.1 MDLs are to be determined for each analyte and for each matrix. This SOP describes procedures for determining MDLs for the generic matrices aqueous, solid, and gaseous. MDLs for specific matrix types may be adapted from the procedures in this SOP. See Section 3.5.1.

6.1.2 All sample processing steps in the analysis procedure shall be included in the determination of the MDL. MDLs shall be generated for all preparatory and cleanup procedures routinely used on samples.

6.1.3 An MDL study is required for PCB Aroclors 1016 and 1260 only; i.e., it is not necessary to perform an MDL study for all the PCB Aroclors, unless required by specific clients or accreditation programs.

6.1.4 An MDL study is not required for any analyte for which spiking solutions or quality control samples are not available; e.g., temperature.

6.2 Frequency of MDL Determination

6.2.1 An MDL study shall be determined initially; i.e., when the procedure is first put into production. An MDL study may also be done as part a procedure's training requirements.

6.2.2 An MDL study shall be performed at the frequency specified in the applicable method or as specified by an accrediting authority. For example, some state accrediting programs require annual MDL studies.

6.2.3 If an MDL study is not performed annually, an MDL verification check shall be performed quarterly[4] on every instrument used to perform a particular analysis. The MDL verification check sample is spiked at approximately two times the current MDL. The MDL verification check sample shall be acceptable if it produces a response that is at least three times above the instrument's noise level. If the MDL verification check fails, additional MDL verification checks shall be performed at a higher level to set a higher MDL, or a new MDL study shall be performed.

6.2.4 A new MDL determination is to be performed "…each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis."[5]

6.3 Estimation of the MDL

Use one of the following guides to help estimate the MDL.

6.3.1 The concentration value that corresponds to an instrument signal-to-noise ratio in the range of 2.5 to 5.

6.3.2 The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

6.3.3 That region of the calibration curve where there is a significant change in sensitivity, i.e., a break in the slope of the calibration curve.

6.3.4 Instrumental limitations.

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[4] The quarterly MDL verification checking procedure is based on the procedure in Reference 9.7, Section D.1.4, Clarification Box D-12.

[5] See Reference 9.6, Section D.1.2.c) and Reference 9.7, Section D.1.4.c).

6.4 Aqueous Blank MDLs

6.4.1 Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at or above the MDL of each analyte of interest.

6.4.2 Prepare a minimum of 7 (preferably 8 to 12) analyte-spiked reagent water samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3.

6.4.3 Analyze the analyte-spiked reagent water samples prepared in Section 6.4.2 by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for water samples.
Proceed to Section 6.10.

6.5 Aqueous Sample MDLs

6.5.1 Analyze the aqueous sample by processing it through the **entire** analytical procedure.

6.5.2 Calculate the analyte concentration.

6.5.2.1 If the measured concentration of the analyte is in the recommended range of 3 to 5 times the estimated MDL from Section 6.3, proceed to Section 6.5.3.

6.5.2.2 If the measured concentration of the analyte is less than the recommended 3 to 5 times the estimated MDL, add a known amount of analyte to bring the concentration of analyte between 3 to 5 times the estimated MDL and proceed to Section 6.5.3.

6.5.2.3 If the measured concentration of the analyte is greater than 5 times the estimated MDL, either obtain another sample with a lower concentration of analyte in the same matrix, or the sample may be used as is for determining the MDL if the analyte concentration does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical procedure changes as the analyte concentration increases from the MDL; hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations. Proceed to Section 6.5.3.

6.5.3 Prepare and analyze a minimum of 7 (preferably 8 to 12) aliquots of the aqueous sample by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for water samples. Proceed to Section 6.10.

6.6 Solid Blank MDLs

6.6.1 Prepare a solid material (e.g., soil, sand, tissue, Na_2SO_4, Teflon chips, or other appropriate material) that is free of analyte.

6.6.2 Prepare a minimum of 7 (preferably 8 to 12) analyte-spiked solid samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3. The same weight of analyte-spiked solid is substituted for the sample weight in the analytical procedure.

6.6.3 Analyze the analyte-spiked solid samples prepared in Section 6.6.2 by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for solid samples. Proceed to Section 6.10.

6.7 Solid Sample MDLs

6.7.1 Analyze the solid sample by processing it through the **entire** analytical procedure.

6.7.2 Calculate the analyte concentration.

6.7.2.1 If the measured concentration of the analyte is in the recommended range of 3 to 5 times the estimated MDL from Section 6.3, proceed to Section 6.7.3.

6.7.2.2 If the measured concentration of the analyte is less than the recommended 3 to 5 times the estimated MDL, add a known amount of analyte to bring the concentration of analyte between 3 to 5 times the estimated MDL and proceed to Section 6.7.3.

6.7.2.3 If the measured concentration of the analyte is greater than 5 times the estimated MDL, either obtain another sample with a lower concentration of analyte in the same matrix, or the sample may be used as is for determining the MDL if the analyte concentration does not exceed 10 times the MDL of the analyte in soil. The variance of the analytical procedure changes as the analyte concentration increases from the MDL; hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.
Proceed to Section 6.7.3.

6.7.3 Prepare and analyze a minimum of 7 (preferably 8 to 12) aliquots of the soil sample by processing them through the **entire** analytical procedure. Make all computations according to the directions prescribed in the analytical procedure with the final results reported in the same units as used for solid samples.
Proceed to Section 6.10.

6.8 Gaseous Blank MDLs

6.8.1 Using an appropriate sample container (e.g., Tedlar® bag or SUMMA® passivated canister) and appropriate analyte-free inert gas (such as zero-grade air or ultrapure nitrogen), prepare a minimum of 7 (preferably 8 to 12) analyte-spiked inert gas samples at a concentration that is 3 to 5 times the estimated MDL from Section 6.3.

6.8.2 Analyze the analyte-spiked inert gas samples prepared in Section 6.8.1 by processing them through the **entire** analytical procedure. Make all computations according to the directions in the analytical procedure with the final results reported in the same units as used for air samples. Proceed to Section 6.10.

6.9 Rejection of Replicate Sample Results

6.9.1 A replicate sample result may only be rejected if there is an assignable cause for not using that result. Assignable causes include, but are not limited to, replicate sample preparation error, instrument malfunction, bad injection or purge, and internal standard(s) missing or response uncharacteristically high or low. The cause for rejecting the replicate sample result must be documented in the MDL data package.

6.9.2 For multi-analyte analyses, if a replicate sample result is rejected for an assignable cause, results for all the analytes from that sample are to be rejected; that is, "picking and choosing" analyte results from a sample is not permitted.

6.10 Calculation of MDL_C

6.10.1 Determine the standard deviation, *s*, of the replicate sample results.

$$s = \sqrt{\frac{\sum_{n=1}^{i} (x_i - \bar{x})^2}{n - 1}}$$

where $\overline{x} = \dfrac{\sum_{n=1}^{i} x_i}{n}$

6.10.2 Multiply the standard deviation obtained in Section 6.10.1 times the appropriate one-sided 99% Student's t-statistic, which is found in the following table.

$MDL_C = s \times$ {appropriate Student's t-statistic}

No. of Samples (n)	Student's t-statistic	Degrees of Freedom (n - 1)
7	3.143	6
8	2.998	7
9	2.896	8
10	2.821	9
11	2.764	10
12	2.718	11
13	2.681	12
14	2.650	13
15	2.624	14
16	2.602	15
17	2.583	16
18	2.567	17
19	2.552	18
20	2.539	19
21	2.528	20

6.11 Determination of MDL_R

The Reported MDL (MDL_R) is the calculated MDL rounded **up** to the appropriate number of significant figures. See Section 3.1.2.

6.12 Evaluation of the Quality of the MDL Study

The quality of the MDL is evaluated using the following criteria.

6.12.1 <u>Spike Level</u> The spike level is **too low** if the MDL_C is greater than the spike level. The spike level is **too high** if the spike level is greater than <u>ten</u> times the MDL_C.

6.12.2 Percent Relative Standard Deviation (%RSD) The %RSD should be some value close to 20, where the %RSD is equal to the standard deviation (*s*) divided by the average of the spike recoveries times 100. [$\%RSD = (s \div \overline{x})\ 100$]

6.12.3 Percent Spike Recovery The spike recovery should be approximately what is to be expected for that analyte from the analytical procedure; i.e., a 40% spike recovery for an analyte is too low if the method normally recovers 80% or more for that analyte.

6.12.4 MDL Quality The criteria in Section 6.12.1 must be true. At least one of the criteria in Sections 6.12.2 and 6.12.3 should also be true. If the MDL_C does not meet these criteria, then the study should be repeated, adjusting the spike level appropriately.

6.13 Instruments

If more than one instrument is used for the same analytical procedure, the replicate samples should be analyzed on each instrument to ensure there is no instrument bias. Under some specific customer contracts and for some programs (such as the Navy's Installation Restoration program), instrument-specific MDLs are required. There are two options for complying with this requirement:

1. Analyze the replicate samples on each instrument used for the analytical procedure and calculate the MDL_C for each instrument. The MDL_R will be the largest of the several MDL_C's; or

2. Analyze the replicate samples on each instrument used for the analytical procedure and calculate a single MDL_C using all the values from each instrument. A minimum of five values is needed from each instrument. For example, if two instruments are used, there would be a minimum of two times five or ten values to be used to calculate the MDL_C. Make sure to use the appropriate Student's t-statistic that corresponds to the number of values used to calculate the standard deviation. Note: This option may not be acceptable under some specific customer contracts or for some programs, such as the DOD quality systems for environmental laboratories.[6]

6.14 Review and Approval

Completed MDL determinations are to be reviewed by the supervisor of the analysis. The QA PM will review and approve the MDL determination before it is implemented.

[6] See Reference 9.7, Section D.1.4.

6.15 Department of Defense (DoD) Requirements[6]

6.15.1 An MDL verification check shall always be performed immediately following an MDL study. DoD requires that the MDL check sample be spiked at approximately 2 times the current reported MDL.

6.15.2 If an annual MDL study is not performed, MDL verification checks shall be performed quarterly. If the quarterly MDL verification check fails, additional MDL verification checks shall be performed at a higher level to set a higher MDL, or the MDL study shall be reconducted.

6.15.3 For DoD, the MDL verification check sample shall be acceptable if it produces a response that lies at least 3 times above the instrument's noise level.

7.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

7.1 Replicate Samples

No fewer then **7** replicate samples can be used; **8** to **12** replicate samples is preferred.

7.2 Analysis of the Replicate Samples

The replicate samples do not have to all be analyzed in the same analytical batch on the same day. In fact, it is preferred to spread out the replicate samples among several analytical batches analyzed on several days (to increase the contribution of the day-to-day variability). Furthermore, it is recommended that at least one MDL spike be routinely analyzed monthly and data accumulated and calculated at a later time.

7.3 MDL Quality

The MDL determination must meet the criteria in Section 6.12. If the MDLs from more than one instrument are combined as in Section 6.13, the combined MDL must meet the criteria in Section 6.12.

7.4 Matrices

MDLs shall be generated for all applicable matrices. See Section 6.1.1.

7.5 Preparatory and Clean-up Procedures

MDLs shall be generated for all preparatory and clean-up procedures routinely used on samples. See Section 6.1.2.

8.0 RECORDS

The data for the MDL determination is summarized in a table similar to the one shown in Figure 1. An Excel spread sheet similar to Figure 1 is available for this purpose. This summary and the reference to the location of the raw data are to be filed in a readily available file of MDLs. This file is to be located both in the department performing the analytical procedure and in a centralized location for MDLs from the entire laboratory. Also shown in Figure 1 are two examples illustrating how MDL data is to be summarized.

9.0 REFERENCES

9.1 *40 CFR Part 136, Appendix B*, Definition and Procedure for the Determination of the Method Detection Limit--Revision 1.11.

9.2 *SOP for Significant Figures*, ADM-SIGFIG.

9.3 *SOP for Sample Batches*, ADM-BATCH.

9.4 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, Third Edition, September 1986 and as amended by Updates I, II, IIA, IIB, III, and IIIA.

9.5 *Standard Methods for the Examination of Water and Wastewater*, APHA/AWWA/WEF, 19th Edition, 1995, Method 1030E; 20th Edition, 1998, Method 1030C.

9.6 National Environmental Laboratory Accreditation Conference (NELAC), Quality Systems Standard, Appendix D, Section D.1.2.

9.7 Department of Defense *Quality Systems Manual for Environmental Laboratories*, Final Version 2, June 2002, Appendix D, Section D.1.4.

10.0 CHANGES FROM PREVIOUS REVISION

- Section 3.1.1 Section 6.10 cross reference corrected
- Section 3.3 Corrected Section number
- Section 3.4 Corrected Section number
- Section 3.5 Corrected Section number
- Section 3.5.1 Changed matrices to generic matrices <u>aqueous</u>, <u>solid</u> and <u>gaseous</u>
- ★ Section 6.1 Section completely revised
- ★ Section 6.2 New section – causing subsequent sections to be renumbered and section cross-references to be revised
- Sections 6.3 through 6.15 Sections renumbered and internal cross references updated
- Section 6.4 “Water” changed to “Aqueous” to be consistent with Section 3.5.1
- Section 6.5 “Water” changed to “Aqueous” to be consistent with Section 3.5.1
- Section 6.7 “Soil” changed to “Solid” to be consistent with Section 3.5.1
- ★ Section 6.12.1 MDL_R changed to MDL_C
- ★ Section 6.12.4 MDL_R changed to MDL_C
- Section 6.13 “Navy’s Installation and Restoration program” changed to “DOD quality systems for environmental laboratories” at end of paragraph 2.
- Section 7.4 Cross reference changed to Section 6.1.1
- Reference 9.7 Updated

Figure 1

MDL Determination Summary

Analytical Method: 8270C Instrument: SVM GC/MS No. 03
Extraction/Digestion Method: 3520C
Matrix: Water / ~~Soil~~ / ~~Air~~ Units: ug/L (ppb)
Analyst(s): I. M. Good

Approved by: ______________________ Date: ____________

		Date Analyzed	1/2/03	1/2/03	1/9/03	1/9/03	2/4/03	2/4/03	2/4/03	2/9/03	2/9/03	3/1/03								
		Instrument Identification	03	03	03	03	03	03	03	03	03	03								
Analyte	Low Std	Spike Level	1	2	3	4	5	6	7	8	9	10	11	12	Mean	Std Dev	%RSD	MDL_C	$\mathbf{MDL_R}$	NOTES
NPTH[1]	20	5.0	4.1	4.8	5.2	5.9	4.9	5.1	5.0	4.5	4.8	5.6			5.0	0.51	10	1.45	**1.5**[3]	
PCP[2]	50	10	6.1	4.8	5.2	4.5	5.8	4.7	4.1	5.1	6.0	4.0			5.0	0.75	15	2.12	**2.2**[3]	

[1] Naphthalene [2] Pentachlorophenol [3] Since these are organic analytes, the MDL is rounded up to two significant figures, per Section 3.1.2.

STANDARD OPERATING PROCEDURE

SAMPLE RECEIVING

SMO-GEN

Revision 2
December 8, 2004

Approved By: ______________________________ ____________
Supervisor Date

______________________________ ____________
QA Coordinator Date

______________________________ ____________
Laboratory Manager Date

One Mustard St., Suite 250
Rochester, NY 14609

Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: ______ Date: __________
Initials: ______ Date: __________
Initials: ______ Date: __________

DOCUMENT CONTROL

NUMBER: ________________

Initials: ______ Date: ________

1 SCOPE AND APPLICATION

This Sample Management SOP provides a key foundation to the SMO department. It explains the process of receiving samples and the steps that lead to the distribution of samples throughout the lab. By implementing an organized and thorough approach to the initial stages of the process, we can maintain an efficient and well-documented account of the samples status and condition.

2 METHOD SUMMARY

The process of receiving and distributing samples is outlined in this SOP. Upon receipt, a CR/PF is completed for each cooler. The sample information is logged into the LIMS database and then broken-down and distributed within the lab.

3 DEFINITIONS

SMO	Sample Management Office
PM	Project Manager
CR/PF	Cooler Receipt & Preservation Form
QA/QC	Quality Assurance / Quality Control
LIMS	Laboratory Information Management System
COC	Chain of Custody
BREAKDOWN	The act of removing samples form coolers, labeling the samples, checking preservations, and distributing them to the correct destinations.
LOG-IN	Entering the information from the COC, CRPF, and the specifics of the job into the LIMS
MATRIX	The physical form of a sample. (water, oil, soil, solid, air)
NELAC	National Environmental Laboratory Accreditation Conference

4 INTERFERENCES

To avoid errors during log-in, detailed information shall be obtained from clients to complete chain of custody documentation.

5 SAFETY

5.1 The characteristics of incoming samples are often unknown. Treat all samples as potentially hazardous. SMO has first contact with samples and must be especially cautious.

5.2 All appropriate safety precautions for handling reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.3 Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4 Hydrochloric and Nitric Acid are used in this method. These acids are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. And safety glasses should be worn while working with the solutions. Lab coat and gloves should always be worn while working with these solutions.

5.5 Refer to the Safety Manual for further discussion of general safety procedures and information.

6 SAMPLE CONTAINERS, COLLECTION, PRESERVATIONS, AND STORAGE

Sample preservation and storage are discussed as part of the procedure later in this SOP.

7 APPARATUS AND EQUIPMENT

- Infrared or digital thermometer – calibrated and maintained as per ADM-DALYCK.

8 PREVENTIVE MAINTENANCE

Not Applicable

9 STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

9.1 The following reagents are purchased commercially, stored at room temperature and expire upon manufacturer's indications or 3 years from receipt if no other indication is given:

Sulfuric Acid; Instranalyzed grade
Nitric Acid; Instranalyzed grade
Hydrochloric Acid; Instranalyzed grade
Sodium Hydroxide; Lab grade

9.2 Consumable materials:
PH indicator Paper
Potassium-Iodide Starch Paper for detection of residual chlorine

10 RESPONSIBILITIES

It is the responsibility of the analyst to receive samples according to this SOP and to complete all documentation required.

11 PROCEDURE

11.1 SAMPLE ACCEPTANCE POLICY

11.1.1 The laboratory's sample acceptance policy outlines the circumstances under which samples shall be accepted or rejected. This information is made available to the sampler by an instruction sheet that accompanies each bottle set sent to the client (attached).

11.1.2 The samples received need to conform to the following acceptance criteria as per NELAC:

- Proper, full, and complete documentation (COCs), which shall include sample identification, the location, date and time of collection, collector's name, preservation type, sample type and any special remarks concerning the sample;
- Proper sample labeling to include unique identification and a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink;
- Use of appropriate sample containers;
- Adherence to specified holding times;
- Adequate sample volume. Sufficient sample volume must be available to perform the necessary tests; and
- Procedures to be used when samples show signs of damage, contamination, and inadequate preservation.

The above criteria are addressed in the rest of this section. In the event of an unacceptable sample, the Project Manager is notified and they will contact the client or recommend a proper course of action. Any data from samples which do not meet the acceptance policy must be written up in the case narrative in the report.

11.2 PROCEDURES FOR SAMPLE RECEIPT

11.2.1 The CAS Cooler Receipt and Preservation Form (CR/PF) (attached) is used for the next steps to document the condition of the samples and coolers as per the Acceptance Policy.

11.2.2 Upon receipt, the coolers are examined for presence and condition of custody seals, locks, shipping bills, etc. The shipping labels are removed and placed on scrap paper and added to the receiving paper work.

11.2.3 The coolers are opened and examined for any existing hazards before subsequent processing.

CAUTION: *If samples exhibit any strong odors, or samples have been damaged, move cooler to the hood and continue processing per client.*

11.2.4 Chain of Custody (COC) forms (attached) and any other documents are located, removed and signed with date & time as received. Visually scan the COC for short holding time samples.

11.2.5 The temperature of the cooler is measured following the guidelines in this SOP. The acceptance criteria for samples is 0-6°C. If a cooler exhibits a temperature greater than 6°C, or exhibits any other anomalies (deviations from the Acceptance Policy), the anomalies are noted on the CR/PF and the CR/PF is placed on top of the COC packet.

11.2.5.1 Samples which are hand delivered immediately after collection (delivered within 4 hours of sampling) may not have had time to cool. The samples are considered acceptable by NELAC if there is evidence that the chilling process has begun. Document the presence of ice on the CR/PF with a note about the 4-hour rule.

11.2.6 Once the coolers are initially examined and observations and temperature are recorded, all of the COCs with corresponding CR/PF forms and shipping labels are submitted for review to the appropriate Project Manager. (The receiving paper work is comprised of at least 3 pages; the COC, a CR/PF, and a shipping label).

11.2.7 Rush requests and samples with short holding times are always given top priority for initial processing. CAS follows EPA guidelines for preservation and holding time as outlined in our QA/QC manual Table 7-1. A list of short holding time parameters are attached to this SOP. An additional list of holding times may be found in SMO-BPS. If short holding time samples need to be distributed immediately (before log-in and labeling), distribute the samples with the attached form for Internal Tracking. Write all short holding time samples on the white board in Wetchem.

11.2.8 In the down time between receiving and actual breakdown of samples, the coolers are stored in the SMO walk-in cooler, which also maintains a temperature of 0-6°C.

11.3 LOG-IN/LIMS

11.3.1 At log-in, the Project Manager enters the entire job into the LIMS system. The job is given a submission number, which consists of the lab location, year, and a unique sequential number. (R20-1508)

11.3.2 Each sample is given a unique order number during log-in. This number is unique to a given location or sample site. A single sample site may consist of many bottles according to the analyses requested. The individual bottles within an order number are uniquely identified with the use of a bar code placed on the bottles during sample breakdown. See SMO-ICOC.

11.3.3 COC' s are returned to SMO after the Project Manager has approved all anomalies (See ADM-PCR) and entered the job into the LIMS database. At this point, the jobs are approved for breakdown.

11.4 SAMPLE BREAKDOWN

11.4.1 Sample containers are removed and organized according to chain of custody identification and analysis.

11.4.2 The following verifications are made as to the agreement of chain of custody information as it applies to samples and containers received:

- Sample identification, time, date
- Number of containers received
- Matrix
- Correct bottles for analysis requested.
- Correct sample volume for analysis
- Correct preservatives for analysis – according to the labels. The actual preservation will be tested as below.

Any discrepancies are reported to the Project Manager. Tests may be added or deleted so that LIMS matches the actual samples received. See the discrepancies section of this SOP (i.e. jobs can not have tests scheduled when the sample containers do not exist.)

11.4.3 Labels are printed from the LIMS database and placed on the sample containers.

11.4.4 Barcodes are generated which are unique to each container for the purpose of sample tracking. VOA bags receive one barcode and each vial within the bag must be labeled with a different number (if not already done so when preparing the bottle set)

11.4.5 Preservations are checked on the appropriate samples and recorded on the job paperwork, the preservation check log, and preservative lot numbers are recorded on the front page of the paper work (the Analytical Request).

11.4.6 To check the preservation, place a small piece of pH test paper in a dispo-cup and pour a small aliquot of the sample into a dispo-cup. Observe the color of the paper and compare to the colors on the paper dispenser to determine the pH. The preservation of samples should be as below:

HCl, HNO_3, H_2SO_4 pH < 2
NaOH pH > 12
PCB 608 pH 5-9

If the sample was not sufficiently preserved, notify the Project Manager to determine whether more preservative should be added.

11.4.7 To check the chlorine residual, place a small piece of starch paper in a dispo-cup and pour a small aliquot of the sample into a dispo-cup (this may be done on the same aliquot used to test pH). If the paper turns blue there is chlorine residual present in the sample. Note the discrepancy on the CR/PC and notify the Project Manager. The Project Manager may contact the client to determine if ascorbic acid should be added to eliminate the chlorine residual.

11.4.8 The CR/PC form is finished by the person who broke down the job.

11.4.9 All of the jobs are reviewed for completeness at the end of the day (or the following morning), and the walk-in cooler temperatures are logged into a temperature logbook.

11.5 SAMPLE DISTRIBUTION

11.5.1 After a job is labeled, the samples are distributed to the appropriate department. The samples are scanned into the appropriate storage areas as listed below.

11.5.2 CAS-Rochester currently maintains 3 walk-in coolers to refrigerate samples. Extractables share a cooler with Metals, VOAs have a cooler, and WetChem shares the cooler with SMO. Metals are maintained at room temperature and are placed on a dedicated cart in the metals department. Mercury and TCLP samples are placed in the Metals/Extractables cooler. SMO is responsible for documenting the location of the Wetchem samples in the Wetchem/SMO cooler.

11.6 SAMPLE SECURITY AND STORAGE:

11.6.1 Bar-coding is used as a means of sample tracking. Custody is maintained according to SMO-ICOC.

11.6.2 The sample coolers are secured with locks, which can be accessed by technical laboratory personnel, project managers, administrative support personnel and all senior staff members. All of the sample storage facilities are located in our building which is a secured area. Storage areas are kept clean and dry to avoid any damage or deterioration of samples while in storage.

11.6.3 Samples are held in refrigerators (if applicable) until analysis is completed and reported to the Client. Routine samples are typically held for 30 days after mailing of report and CLP samples are stored for 90 days after report has been mailed.

11.6.4 Refrigeration is maintained at a temperature of 0-6° Celsius.

11.7 <u>DISCREPANCIES</u>

11.7.1 Any discrepancies or concerns such as non-matching identifications, missing samples, and tests not scheduled correctly are to be verbally communicated to the Project Manager. Any action taken is recorded on the COC and/or cooler receipt form, "as per" Project Manager. The Project Manager will make any contact to the client when they deem it necessary. If a Chain of Custody is not received, the Project Manager is informed and a CAS COC is filled out.

11.7.2 In the event of broken samples, a note is entered on the Chain of Custody and/or the CR/PF accompanying the samples. Information pertaining to the sample is forwarded to the Project Manager for follow up purposes. Cleanup procedures are as follows:

- Liquids: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. The liquid is disposed of in the SMO sink or under a hood if strong odors are evident. Any packing material is disposed of appropriately.

- Soils: The same documentation as liquids applies. Broken glass is disposed of in the Glass Disposal Box and the soil is disposed of into the garbage.

11.8 <u>RECEIVING SAMPLE COOLERS ON WEEKENDS OR AFTER HOURS</u>

11.8.1 The date received is the date on which the Laboratory Personnel takes possession of the samples. The client shall sign the COC as relinquished and the CAS employee shall sign in the adjacent box as received. If an employee outside of the SMO department receives the samples, the coolers or samples are stored in a locked walk-in cooler and all paperwork is left on the lab bench in SMO for login the next working day.

11.8.2 If the samples are received by SMO staff but the samples cannot be processed through the complete log-in procedure on the date received, the receiving procedure is performed as outlined in 11.1 and 11.2. Then SMO needs to check for short holding time samples. Short holding time tests are posted in breakdown. Most of the tests have holding times of 48 hours which means samples received on Saturday need to be run before Monday. Any cooler integrity issues shall be handled on the next business day, but the samples need to be tested so that holding times are maintained. To maintain an organized system, notes are indicated on the COC and on the white board in Wetchem as to which samples have been sent for analysis. Use the attached form for Internal Tracking of Short holding time samples.

11.9 SAMPLE SHIPPING TO SUBCONTRACT LABS

11.9.1 The sample is logged in and the test code for subcontracted analysis is assigned.

11.9.2 For CAS Network Labs: Subcontracted samples are shipped to the network lab with a copy of the Internal Service Request form (ISR) and copy of the COC. The tests being subcontracted must be highlighted and the number of containers adjusted or a new COC is completed.

11.9.3 For other labs: A purchase order (PO) is filled out for work going to another contract laboratory. TAT, deliverables, etc. should be clearly specified. A new Chain of Custody form is filled out with the pertinent information so the samples can be analyzed in a fashion that meets the client's needs.

11.9.4 Samples are prepared for shipping by packing in bubble wrap, and ice. Temperature blanks, and the chain of custody are placed in shipping coolers. Custody seals are signed and dated and placed on the front of the cooler. The cooler is then sealed with packaging tape and shipped overnight through the courier system (confirm with Project Manager for am or pm delivery requirements).

11.10 THERMOMETER MEASUREMENTS

11.10.1 Unless unavailable, measure the cooler/sample temperature of an incoming cooler with the Infrared (IR) thermometer. Turn on the thermometer and point it at the temp blank or a sample (preferably clear glass or amber glass). Wipe the container with a dry paper towel. Hold the thermometer approximately 3-6 inches from the container and at least 3 inches above the counter. Temperature is rounded to the nearest whole number and recorded to the nearest whole number on the cooler receipt form and COC. This method is preferred to the digital thermometer method.

11.10.2 If the IR thermometer is not available, a digital thermometer may be used. Place the thermometer in the temperature blank or plunge it into the packing material or place it as deep into the cooler as is practical with the lid closed. Allow to equilibrate 5 minutes. After measurement, the temperature is recorded to the nearest whole number in the appropriate space on the cooler receipt form and COC.

12 QA/QC REQUIREMENTS

12.1 Not Applicable

13 DATA REDUCTION AND REPORTING

13.1 All samples, custody documents and discrepancy forms must be clearly completed with permanent ink and filed with the project folder.

14 WASTE MANAGEMENT AND POLLUTION PREVENTION

14.1 Not applicable.

15 REFERENCES

15.1 *Test Methods for Solid and Hazardous Waste Physical and Chemical Analyses*, USEPA SW846, December 1996.

15.2 NYSDEC *Analytical Services Protocol*, October 1995.

15.3 NELAC Standard, Chapter 5, July 2002.

16 TRAINING OUTLINE

- Read this SOP.
- Follow policies in ADM-TRANDOC.
- Observe performance of this SOP. Follow Breakdown Training Plan Form.
- Perform this SOP with guidance.
- Perform this SOP independently and have a trained analyst check the trainee's work. If work is acceptable, complete Training Plan Form and file with QA.

17 INSTRUMENT-SPECIFIC ADDENDUM

Not Applicable

18 ATTACHMENTS

18.1 Sampling Instructions

18.2 Short Holding Time Parameters List

18.3 Cooler Receipt and Preservation Form

18.4 COC: Chain of Custody

18.5 Internal Tracking Form for Short Holding Time Samples.

19 CHANGES FROM PREVIOUS REVISION

- 3 – Added Definition of Log-In
- 5 – Modified Safety for consistency with other SOPs
- 9 – Added pH paper and KI-Starch paper to supplies
- 11.2.4 Added need to check COC for shorties
- 11.2.5 Eliminated that discrepancies are highlighted in yellow on COC
- 11.2.7 Added procedure if shorties need done before log-in
- 11.3.2 Added reference to SMO-ICOC
- 11.3.3 Added reference to ADM-PCR
- 11.4.2 Moved preservative requirements out of this section and into (new) 11.4.6+.7
- 11.4.6 +.7 Added detail of how to check preservatives
- 11.5 Simplified wording – eliminated the holding cart. Added that SMO responsible for documenting the location of samples in cooler
- 11.6 Eliminated wording about paper chains and phasing in barcoding
- 11.8.2 Changed white board from SMO to WC
- 11.9.4 Changed from UPS to "courier"
- 11.10.1 Changed the use of the IR gun distance from 7-12 inches to 3-6 inches. Added need to wipe container with a dry paper towel when using IR gun.
- 15 Changed NELAC reference from 1999 to 2002.

SAMPLING INSTRUCTIONS

1. Please Use Caution! Some bottles contain Preservatives such as Acids and Bases that are CORROSIVE! These bottles are marked with colored stickers to inform the sampler but gloves should be worn at all times during sampling for your own protection. (preservative information is on the flip side for emergencies)

2. Please overfill VOA vials and stoppered bottles to eliminate headspace that interferes in the analysis of the samples – but do not overfill too much or the preservative will be flushed out.

3. Please use all of the containers that we provide for a sampling location. This will ensure that the proper containers and volumes are returned for the tests that were requested.

4. Vials labeled TRIP BLANK or TB are included in each cooler containing vials used for testing volatile organics. These vials are a control to determine if the cooler was exposed to contamination while in route or during sampling. Please indicate on the Chain of Custody if you wish to have these vials tested.

Returning Coolers Checklist – Please Read!

Incomplete information will result in a phone call and hence delayed processing of your samples.

1. ***Labeling*** all bottles or soil jars is essential. We look for a **location ID**, a **date**, a **time, initials, preservation, and sample type** on all bottles to verify a location against the Chain of Custody. (Remember that ice water can smudge or remove your makings. a permanent marker on a dry bottle works best)

2. The ***Chain of Custody*** should include: the **client information and sampler's signature** in the top left box, the **location ID**'s of the sample with the **analysis and preservation** indicated in the center section, **turn-around-time and reporting** information in the bottom center section, and **sign-off** (signature/date/time) to the courier on the bottom left section.

3. ***Custody stickers*** are very important for CLP or ASP package work and are encouraged for all coolers. The sticker should be placed over the lid and body of the cooler and taped securely. These stickers provide an added level of security, and if they are broken when the coolers arrive at CAS, we will contact you.

4. ***Packaging coolers*** well is a key to avoid resampling. Beware of glass and make sure they are in the bubble bags that we provide. Also a snug fit is suggested. Extra paper or cardboard (especially with amber liters) is encouraged. **Note** that when the ice melts, the bottles can move inside of the cooler. **Any Leaking Coolers in shipment will be considered HAZARDOUS** by the courier (UPS). Please seal the cooler with packing tape and/or place samples and ice in a plastic bag in the cooler. A leaking cooler will likely result in a delay at UPS and missed holding times at the LAB.

5. ***Receiving Temperature at CAS*** is a key element to the validity of your results to withstand scrutiny in a court of law. Our Data is only considered valid if the samples have a temperature of 6 degrees Celsius or less. A temperature blank is include in all coolers and should be returned in ice with the other samples. Ice should be bagged **or** put the ice and samples in a large plastic bag and tie it off to reduce leakage. Submersion is the best way to cool the samples but watch out for labels falling off or smudging.

6. ***Your supplies*** (like coolers or icepacks) will gladly be returned if we have complete return-address information! Please document **your return-address on the cooler** or ice packs in the form of a sticker, or permanent marker so we can return your supplies.

7. ***Ship samples*** using overnight service or deliver within 24 hours of sampling time. If shipping for **Saturday**, Check mark the Saturday-delivery Box and <u>you must</u> affix several "Saturday" stickers to the cooler.

SHORT HOLDING TIMES

BREAK DOWN:	HOLDING TIME	WHEN
pH	ASAP	Run daily
Conductivity	48hr from sample date	Run daily
Color	48hr from sample date	Run as needed
Turbidity	48hr from sample date	Run as needed
Sett. Solids	48hr from sample date	Run Same day

WET CHEM:

BOD	Wed./Friday	48hr from sample date
NO3	ASAP (IC)	48hr from sample date
NO2	ASAP (lachat)	48hr from sample date
Residual Chlorine	ASAP	
Odor	ASAP	
Dissolved Oxygen	ASAP	
Coliform test	ASAP (Bev)	
Orthophosphate	ASAP	48hr from sample date
Chrome Hex	ASAP	24hr from sample date
Surfactants	ASAP	48hr from sample date
Ferrous Iron	ASAP	24hr from sample date
TSS,TDS,TS,TVS	(ck sample date 7 days)	
Sulfite	ASAP	
Sulfides	(ck sample date 7 days)	

Cooler Receipt And Preservation Check Form

Project/Client______________________________Submission Number__________________.

Cooler received on__________ by:________**COURIER:** CAS UPS FEDEX CD&L CLIENT

1.	Were custody seals on outside of cooler?	YES	NO	
2.	Were custody papers properly filled out (ink, signed, etc.)?	YES	NO	
3.	Did all bottles arrive in good condition (unbroken)?	YES	NO	
4.	Did any VOA vials have significant air bubbles?	YES	NO	N/A
5.	Were **Ice** or **Ice packs** present?	YES	NO	
6.	Where did the bottles originate?	CAS/ROC,	CLIENT	
7.	Temperature of cooler(s) upon receipt:			

Temperature of cooler(s) upon receipt: _______ _______ _______ _______ _______

Is the temperature within 0° - 6° C?:	Yes	Yes	Yes	Yes	Yes
If No, Explain Below	No	No	No	No	No

Date/Time Temperatures Taken: ______________________________________

Thermometer ID: 161 or IR GUN Reading From: Temp Blank or Sample Bottle

If out of Temperature, Client Approval to Run Samples______________________________

Cooler Breakdown: Date :____________________________by:______________________

1.	Were all bottle labels complete (*i.e.* analysis, preservation, etc.)?	YES	NO
2.	Did all bottle labels and tags agree with custody papers?	YES	NO
3.	Were correct containers used for the tests indicated?	YES	NO

4. Air Samples: Cassettes / Tubes Intact Canisters Pressurized Tedlar® Bags Inflated N/A

Explain any discrepancies: ____

		YES	NO	Sample I.D.	Reagent	Vol. Added
pH	Reagent					
12	NaOH					
2	HNO_3					
2	H_2SO_4					
Residual Chlorine (+/-)	for TCN & Phenol					
5-9**	P/PCBs (608 only)					

YES = All samples OK NO = Samples were preserved at lab as listed PC OK to adjust pH__________

**If pH adjustment is required, use NaOH and/or H_2SO_4

VOC Vial pH Verification (Tested after Analysis) Following Samples Exhibited pH > 2				

Other Comments:

Columbia Analytical Services INC.
An Employee - Owned Company
www.caslab.com

CHAIN OF CUSTODY/LABORATORY ANALYSIS REQUEST FORM

One Mustard St., Suite 250 • Rochester, NY 14609-0859 • (585) 288-5380 • 800-695-7222 x11 • FAX (585) 288-8475 PAGE ______ OF ______

SR #

CAS Contact

Project Name	Project Number
Project Manager	Report CC
Company/Address	
Phone #	FAX#
Sampler's Signature	Sampler's Printed Name

ANALYSIS REQUESTED ***(Include Method Number and Container Preservative)***

PRESERVATIVE

CLIENT SAMPLE ID	FOR OFFICE USE ONLY LAB ID	SAMPLING DATE	SAMPLING TIME	MATRIX	NUMBER OF CONTAINERS	GC/MS VOA's ☐ 8260 ☐ 624 ☐ CLP	GC/MS SVOA's ☐ 8270 ☐ 625 ☐ CLP	GC VOA's ☐ 8021 ☐ 601/602	PESTICIDES ☐ 8081 ☐ 608 ☐ CLP	PCB's ☐ 8082 ☐ 608 ☐ CLP	METALS, TOTAL (List in comments below)	METALS, DISSOLVED (List in comments below)								REMARKS/ ALTERNATE DESCRIPTION

Preservative Key
0. NONE
1. HCL
2. HNO_3
3. H_2SO_4
4. NaOH
5. Zn. Acetate
6. MeOH
7. $NaHSO_4$
8. Other ______

SPECIAL INSTRUCTIONS/COMMENTS
Metals

See QAPP ☐

TURNAROUND REQUIREMENTS
____ **RUSH** (SURCHARGES APPLY)
____ **24 hr** ____ **48 hr** ____ **5 day**
____ **STANDARD**
REQUESTED FAX DATE
______
REQUESTED REPORT DATE
______

REPORT REQUIREMENTS
____ I. Results Only
____ II. Results + QC Summaries (LCS, DUP, MS/MSD as required)
____ III. Results + QC and Calibration Summaries
____ IV. Data Validation Report with Raw Data
____ V. Specialized Forms / Custom Report
Edata ____ Yes ____ No

INVOICE INFORMATION
PO#
BILL TO:
SUBMISSION #:

SAMPLE RECEIPT: CONDITION/COOLER TEMP: ______ CUSTODY SEALS: Y N

RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY	RELINQUISHED BY	RECEIVED BY
Signature	Signature	Signature	Signature	Signature	Signature
Printed Name	Printed Name	Printed Name	Printed Name	Printed Name	Printed Name
Firm	Firm	Firm	Firm	Firm	Firm
Date/Time	Date/Time	Date/Time	Date/Time	Date/Time	Date/Time

Distribution: White - Return to Originator; Yellow - Lab Copy; Pink - Retained by Client

SCOC-1102-08

INTERNAL TRACKING FOR SHORT HOLDING TIME SAMPLES

DATE : ____________

TIME : ____________

CLIENT : ____________

SUBMISSION # : ____________

SAMPLE ID	TEST	RELINQUISH SMO Initial	RECEIVED WC Initial	Barcoded	SAMPLE RETURNED Initial / Date / Time

ATTACHMENT D-2

GENERAL ENGINEERING LABORATORIES, LLC

STANDARD OPERATING PROCEDURES

GL-RAD-A-008, Rev. 8	**The Determination of Radium-226**
GL-RAD-A-009, Rev. 11	**The Determination of Radium-228**
GL-RAD-A-011, Rev. 14	**The Isotopic Determination of Americium, Curium, Plutonium, and Uranium**
GL-GC-E-119, Rev. 0	**Particle Size of Soils**
GL-GC-E-064, Rev. 3	**Density**
GL-SR-E-001, Rev. 17	**Sample Receipt, Login and Storage**
GL-MA-E-008, Rev. 11	**Acid Digestion of Total Metals in Aqueous Samples and Extracts for Analysis by ICP or ICP-MS.**
GL-MA-E-009, Rev. 12	**Acid Digestion of Sediments, Sludges and Soils.**
GL-MA-E-014, Rev. 9	**The Determination of Metals by ICP-MS**

ATTACHMENT D-2

GENERAL ENGINEERING LABORATORIES, LLC
STANDARD OPERATING PROCEDURES

GL-RAD-A-008, Rev. 8	**The Determination of Radium-226**
GL-RAD-A-009, Rev. 11	**The Determination of Radium-228**
GL-RAD-A-011, Rev. 14	**The Isotopic Determination of Americium, Curium, Plutonium, and Uranium**
GL-GC-E-119, Rev. 0	**Particle Size of Soils**
GL-GC-E-064, Rev. 3	**Density**
GL-SR-E-001, Rev. 17	**Sample Receipt, Login and Storage**

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF RADIUM-226

(GL-RAD-A-008 REVISION 8)

APPLICABLE TO METHOD:
EPA 600/4-80-032 Method 903.1 (Modified)

TABLE OF CONTENTS

1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF RADIUM-226

2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for Radium-226 in various matrices.

2.2 This method has been modified on the basis of GEL's Performance Based Measurement System (PBMS).

2.3 Solid matrices are decomposed by digestion in accordance with GL-RAD-A-015 for Digestion for Soil and Sand. The digestate is evaporated to dryness and diluted to known volume with nitric acid solution. A stream of helium gas is purged through the sample to initially remove radon from a water sample or solid sample digestate. The sample is then sealed and radon is allowed to ingrow. The radon, which is supported entirely by Ra-226 in the sample, is then purged with helium and trapped on a liquid nitrogen cold trap. The trap is sealed and warmed. The radon is then transferred by vacuum to a Lucas cell and counted after three hours in the cell.

3.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

3.1 General Engineering Laboratories, LLC (GEL) utilizes methods that are derived from established sources. This method has been modified from the source method EPA 600/4-80-032 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," August 1980, Method 903.1, and uses the same principles of radiochemical concentration and counting.

4.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 Batch: environmental samples, which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.2 Method Blank (MB): a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures.

5.3 Laboratory Duplicate (DUP): aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

5.4 Matrix Spike (MS): prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available.

5.5 Matrix Spike Duplicate (MSD): a second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.

5.6 Laboratory Control Sample (LCS): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes.

5.7 Deionized (DI) water: Type II water

6.0 INTERFERENCES

The analysis of samples for Ra-226 content by Rn-222 emanation is very specific using this procedure, and the separation of radium from other elements is not required. Sample losses can occur only as the result of improper sample transfer. Due to the specific nature of Ra-226 measurement by this method, the use of stable barium carrier or radioactive Ba-133 tracer for yield monitoring is not required.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained to the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

7.4 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

Apparatus and Equipment

8.1 De-emanation system with cold trap

8.2 Liquid nitrogen Dewars

8.3 1 Liter plastic bottles

8.4 Amber latex tubing

8.5 Small tubing clamps

8.6 Lucas cells

8.7 Teflon beakers

8.8 HI-pore diffusers

8.9 Graduated cylinder 500 mL

Instrumentation

8.10 Radon flask counter with scalar

9.0 REAGENTS AND STANDARDS

Reagents

All chemicals should be of reagent grade or equivalent whenever they are commercially available.

9.1 Deionized water (DI): Type II water

9.2 Concentrated nitric acid (HNO_3)

9.3 Boric acid, granular, A.C.S. grade

9.4 Liquid nitrogen (LN)

Standards

9.5 NIST traceable Ra-226 standard

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Water samples should be collected in plastic bottles and preserved with concentrated nitric acid to pH 2.

10.2 Before beginning an analysis the analyst should check the sample pH with a pH strip. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with nitric acid to a pH=1-2. If the sample is pH adjusted let the sample sit in the original container for a minimum of 24 hours before analysis.

11.0 SAMPLE PREPARATION

11.1 Solid matrices

NOTE: Alternatively, Ra-226 analysis in solid matrices can be completed as detailed in the Gamma Spectroscopy SOP, GL-RAD-A-013.

11.1.1 For analyses that require sample dissolution, digest solid samples as detailed in GL-RAD-A-015.

11.1.2 Dissolve the sample residue in 5 mL conc. nitric acid and transfer to a labeled de-emanation bottle. Dilute to 500 mL with DI water.

11.1.4 Proceed to Step 11.2 of this procedure.

11.2 Water samples

11.2.1 Transfer 500 mL of sample to a de-emanation bottle.

11.2.2 To remove radon from the sample, purge for at least 30 minutes with helium at a flow rate vigorous enough to remove radon from sample.

11.2.3 At the end of the degassing, seal the sample by connecting the inlet and outlet lines together. Record the END date and time of the initial degassing on the sample Que sheet. Allow the sample to ingrow for a minimum of three days.

NOTE: Before proceeding to Step 11.2.4, it is advisable to begin acquiring background checks on the Lucas cells that will be used during the degassing process.

11.2.4 Fill the Dewars with liquid nitrogen. Lift the platform holding the Dewars to completely submerge the cold trap in LN. Allow the cold trap to equilibrate before proceeding.

11.2.5 Refer to Figure 1 for Operation of Radon Emanation Line. Connect the sample to lines V-3 and V-4 and ensure that the connections are secure. Turn valves V-3 and V-4 to the sample position. Bubbles should be visible as the helium is now purging the radon into the cold trap. Monitor the flowmeter. Allow the helium to flow for 15 minutes. Afterwards, record the date and time of the sample de-emanation.

11.2.6 After 15 minutes, turn valves V-5 and V-6 to the closed position. This will seal the cold trap that now contains the sample radon. The cold trap contains brass filings to create surface area for radon condensation. Turn valves V-3 and V-4 to the bypass position.

11.2.7 Connect the Lucas cell to the system. Pull a vacuum on the system by turning on the vacuum pump and opening valve V-7. With the cold trap still under LN quickly open and close valve V-6 to remove excess helium.

11.2.8 Ensure that valves V-5 and V-6 are closed. Pull a vacuum on the system and the Lucas cell by turning on the vacuum pump and opening valve V-7.

11.2.9 Close valve V-7 and turn off the vacuum pump. Check the system for leaks by observing the vacuum gauge for 30 seconds. The vacuum gauge should hold at the vacuum at the -20 to -30 vac range. If the vacuum does not hold, notify your Group Leader or Team Leader.

11.2.10 Remove the LN Dewar and gently warm the trap with a hot air gun. The trap should feel warm to the touch before proceeding.

11.2.11 Open valve V-6 to the vacuum system. Place hands on valves V-5 and V-6.

Keep eyes on the vacuum gauge. Open valve V-5 and close valve V-6 just before the vacuum pressure goes to zero.

NOTE: The pressure will drop fast so be alert to the clockwise direction required to close valve V-6.

NOTE: If the zero (atmospheric pressure) is slightly passed the sample may still be counted. The analyst is trying to avoid creating a large positive pressure within the Lucas cell, which may cause the cell to leak or rupture.

11.2.12 Allow the radon to equilibrate in the line for 30 seconds. Disconnect the Lucas cell and allow the radon daughters to equilibrate for a minimum of three hours before counting the cell. Place the cell in the counter for 5 minutes before beginning the sample count.

11.2.13 Count each sample for a minimum of 15 minutes. Record the date and time the count is started, the count time and the gross counts observed.

11.2.14 The Lucas cell should be cleaned as soon as possible after the sample count is completed. The Lucas cell cleaning apparatus is connected to the helium and the vacuum.

11.2.15 Connect the Lucas cell to the cleaning apparatus. Turn on the vacuum pump and the helium inlet valve. Turn on the relay to flush and evacuate the cell for at least two minutes.

11.2.16 Store the cell under a slightly positive helium pressure until the next use. The cell should be stored for a minimum of three hours prior to use for sample analysis.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

12.1 A matrix spike (MS) should be run with each batch of 20 or less samples. The recovery of the spike should fall between 75 and 125%. Recovery is calculated as follows:

$$\%\mathrm{Re}c = \frac{spike(pCi/unit) - sample(pCi/unit)}{spikeconcentration(pCi/unit)} * 100$$

12.2 A duplicate sample should be run with each batch of 20 or less samples. The relative percent difference (RPD) between the duplicate (dup) and the sample should be less than or equal to 20%. The RPD is calculated as follows:

$$RPD = \frac{highdup(pCi/unit) - lowdup(pCi/unit)}{Average(pCi/unit)} * 100$$

12.3 A method blank should accompany each batch of 20 or less samples. The reported value should be less than or equal to the CRDL (contract required detection limit).

12.4 A laboratory control sample (LCS) should be run with each batch of 20 or less samples. The recovery of the LCS should fall between 75-125%. The recovery is calculated as follows:

$$\%\mathrm{Rec} = \frac{Observed(pCi/unit)}{Known(pCi/unit)} * 100$$

12.5 Actions required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 12.1 through 12.4 cannot be satisfied, the analyst should inform their group leader and initiate a Nonconformance Report as outlined in "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

NOTE: Client contractual QC requirements override the requirements in this section.

13.0 INSTRUMENT, CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Ludlum Model 2000 operating voltage, plateau generation and standard deviation:

13.1.1 Place a sealed Lucas Cell Ra-226 source of sufficient activity on the detector 5 minutes before counting. Set the front panel discriminator to 50 volts. Count the source and record the counts.

13.1.2 Step the front panel discriminator up in 50-volt increments and acquire counts at the increasing voltages up to 2000 volts and record counts. Plot the gross counts on the y-axis and the voltage on the x axis and determine the “knee” of the plateau.

13.1.3 The knee is determined by drawing straight lines along the rising slope and the plateau portions of the curve. The knee is the point where these two lines intersect. The operating voltage should be selected at 50 – 150 volts above the “knee.”

13.1.4 Put a copy of the plateau for model 2000 scaler/radon flask counter in the Ra-226 Calibration File.

13.1.5 To determine the control limits (standard deviation), place a sealed Lucas Cell Ra 226 source of sufficient activity on the detector. Acquire twenty counts and record each count. If the operating voltage remains the same there is no need to establish new control limits.

13.1.6 Put a copy of the counts and calculation of standard deviation in the Ra-226 Calibration File.

13.2 Calibration, cell constant, efficiency and verification of the Lucas Cell.

13.2.1 Determine what cells need to be calibrated. Either a year from the last calibration or new Lucas Cells. Give yourself at least 3 weeks before old calibration has expired.

13.2.2 Each Lucas Cell needs to be given a two or three digit number (old numbers can be reused). With the first number to each cell will be the detector and rig it goes to. (For example, 120 will go into detector 1 and rig 1, 220 will go into detector 2 and rig 2.) Each lucas cell has one detector it can be counted on and one rig that it can be transferred on.

13.2.3 A background count is performed on each cell before every calibration and verification run and each count is recorded in the logbook.

13.2.4 Each counting cell is calibrated by spiking a 500 mL DI-water sample with a known dpm of Ra-226 activity. The sample is carried through the entire procedure. The procedure is performed 3 separate times to each cell. Record each count.

13.2.5 Put information from the three runs in an excel spreadsheet to calculate cell constant, average and standard deviation. Standard deviation needs to be less than 10 % of the cell constant average. Put the Ra-226 cell constant spreadsheet in the Calibration File.

13.2.6 Each counting cell will be verified by spiking 500 mL of DI-water. Each verification sample is carried through the entire procedure. Acceptance criteria is 100% ± 25%.

13.2.7 After processing verification, put the spreadsheet into the Ra-226 Calibration File.

13.2.8 When calibration file is complete, go into CELLEFF File and change the old cell efficiency to the new cell efficiency.

14.0 ANALYSIS AND INSTRUMENT OPERATION

Refer to "Ludlum Model 2000 Lucas Cell Counter Operating Instructions" (GL-RAD-I-007) for instrument operating instructions.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Refer to "Ludlum Model 2000 Lucas Cell Counter Operating Instructions" (GL-RAD-I-007)

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

16.1 The spreadsheet will calculate the Ra-226 activity, uncertainty, and MDA in pCi/L by the following equation:

$$Ra-226(pCi/unit) = \frac{cpm_s - cpm_b}{2.22 * V * E * I_1 * I_2 * I_3}$$

$$Uncertainty\ (pCi/unit) = \frac{1.96 * \sqrt{\frac{cpm_b}{T_b} + \frac{cpm_s}{T_s}}}{2.22 * V * E * I_1 * I_2 * I_3}$$

Lower limit of detection (lld):

$$MDA\,(pCi/unit) = \frac{2.71 + 4.66 * \sqrt{cpm_b * T_S}}{(2.22 * E * V * I_1 * I_2 * I_3 * T_S\ )}$$

Where:

CPM_s= gross count rate (counts per minute) at the alpha detector voltage plateau.
CPM_b= background count rate for the cell used for counting.
V = volume of sample aliquot (Liters or grams)
2.22 = conversion factor from dpm/pCi
E = counting efficiency of the cell, detector and de-emanation system.
I_1 = $1\text{-}_E\text{-}\lambda t_1$ where λ = decay constant for radon-222 (0.181d $^{-1}$) and T_1= time between initial and final de-emanation in days.
I_2 = $_E\text{-}\lambda t_2$ where λ = decay constant for radon-222 in hours = 0.00755 hr. and and t_2= delay time in hours between 2nd de-emanation and sample counting.
I_3 = $1\text{-}_E\text{-}\lambda t_3/t_3$ where λ = decay constant for radon-222 (0.181d $^{-1}$) and T_3= sample count time in minutes.
T_S = Sample count time in minutes
T_B = Background count time in minutes

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data is reviewed and packaged in accordance with GL-RAD-D-003 for Data Review and Packaging.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

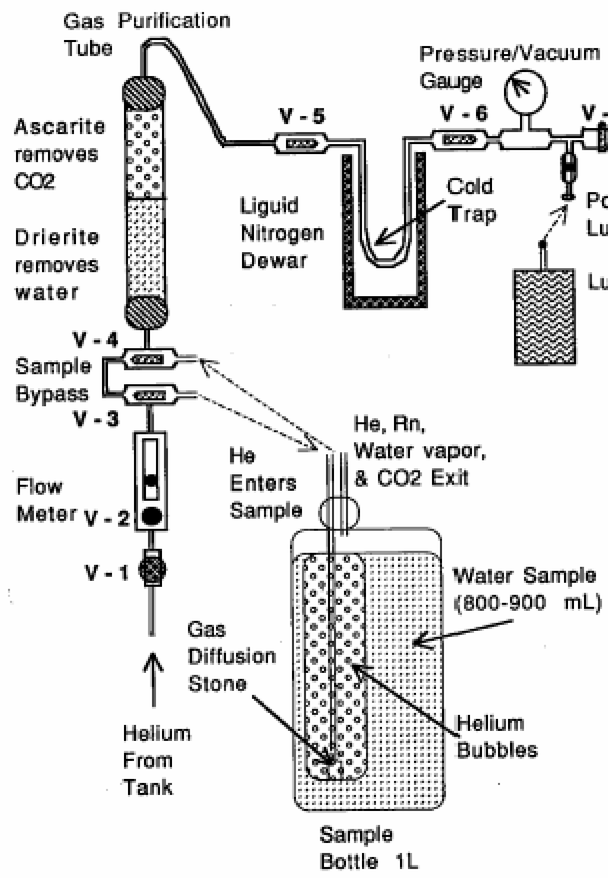
20.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, USEPA, Method 903.1, August 1980.

20.2 Mathieu, G.G., Biscaye, P.E., Lupton, R.A. "A System for Measurement of Rn-222 at Low Levels in Natural Waters." Health Physics, Vol. 55, No.6, pp. 989-992. 1988.

20.3 Key, R.M., Brewer, R.L., Stockwell, J.H., Guinasso, N.L., Schink, D.R., "Some Improved Techniques for Measuring Radon and Radium in Marine Sediments and Seawater. Marine Chemistry, pp. 251-264. October 30, 1978.

20.4 Special thanks to Dr Bill Burnett and his associates at Florida State University for their help in building the radon de-emanation system.

FIGURE 1



Operation of Radon Emanation Line

Intial Degassing

Attach sample to line (He bubbler to valve 3, He exit to hood)
Close Valve 4 (vertical), Open valves 1 & 3 (to the right)
Adjust Valve 2 to 0.4 L/min.
Degass sample for 30 min. , clamp off sample ports
Record Date & Time at the end of degassing

Running Sample

Attach sample to line (He bubbler to valve 3, He exit to valve 4)
Adjust regulator on He tank to 5 lbs.
Open Valves 1, 5, & 6 (5 & 6 Horizontal)
Set Valves 3 & 4 to Sample Bypass (Horizontal , to the left)
Adjust Valve 2 to 0.4 L/min.
Establish He flow for several min. and attach liquid nitrogen dewar
Top-up nitrogen dewar
Start sample deemanation by opening valves 3 & 4 to the sample simultaneously (both horizontal to the right)
Monitor flowmeter, keep at 0.4 L/min.
Degas sample for 30 min.
Close valves 5 & 6
Detach sample (Record Date & Time at the end of degassing)
Attach Lucas cell to filling port
Open Valve 7 to evacuate cell, quickly open and close Valve 6 (1-2 sec.)
Close Valve 7
Remove liquid nitrogen and heat cold trap until warm to the touch
Open Valve 2 (1 or 2 turns counterclockwise)
Open Valve 6
Open Valve 5 and quickly close Valve 6 when gauge reads zero
Remove lucas cell after 2 min. and count after 3 or more hours

FIGURE 1

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF RADIUM-228

(GL-RAD-A-009 REVISION 11)

APPLICABLE TO METHOD:
EPA520/5-84-006, Method Ra-05 (Modified)
EPA 600/4-80-032, Method 904.0 (Modified)

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF RA-228

2.0 METHOD OBJECTIVE, PURPOSE, CODE AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for Radium-228 in water.

2.2 The modifications to this method are based on GEL's Performance Based Measurement System (PBMS).

3.0 METHOD SCOPE, APPLICABILITY AND DETECTION LIMIT

Although this method has been modified from EPA 600/4-80-032 Method 904.0 and EPA 520/5-84-006, Method Ra-05, it uses the same principles of final source preparation, radiochemical concentration and counting. This method is also similar in concept to the source method from "Radiochemical Analytical Procedures for Analysis of Environmental Samples," EPA Environmental Monitoring and Support Laboratory, Las Vegas, 1979.

4.0 METHOD VARIATIONS

Some Variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group Leader or Team Leader. Variations to a method will be documented with the analytical raw data.

5.0 DEFINITIONS

5.1 Batch: environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents.

5.2 Method Blank (MB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus

5.3 Laboratory Duplicate (DUP): aliquots of a sample taken from the same container and processed and analyzed identically but independently.

5.4 Matrix Spike (MS): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations.

5.5 Matrix Spike Duplicate (MSD): a second replicate matrix spike, prepared in the laboratory and analyzed to measure precision and accuracy of the analytes of interest.

5.6 Laboratory Control Standard (LCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

5.7 Deionized Water (DI): Type II water

6.0 INTERFERENCES

6.1 When converting barium sulfate to the carbonate it is important to remove excess sulfate or the potassium carbonate will be consumed by the reaction:

$$K_2CO_3 + H_2SO_4 \;\text{-->}\; K_2SO_4 + H_2O + CO_2$$

6.2 Samples with high strontium-90 may cause interference in the Ac-228 beta count. This problem occurs because of Y-90 present that may follow the Ac-228 chemically. It is best to confirm high Ra-228 (i.e. greater than 5 pCi/L) by gamma spectroscopy.

6.3 Samples with elevated radio lead may cause interference in the Ac-228 beta count. It is best to confirm high Ra-228 (i.e. greater than 5 pCi/L) by gamma spectroscopy.

6.4 Th-234 would potentially interfere with Ac-228 beta counting. Its presence could be confirmed with a decay curve analysis.

7.0 SAFETY PRECAUTIONS AND WARNINGS

7.1 Personnel performing this analytical procedure are trained to the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

7.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

7.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

7.4 If there is any question regarding the safety of any laboratory practice, STOP IMMEDIATELY and consult qualified senior personnel such as a Group or Team Leader.

8.0 APPARATUS, EQUIPMENT AND INSTRUMENTATION

8.1 Apparatus and Equipment

8.1.1 Pyrex watch glasses
8.1.2 Centrifuge
8.1.3 50 mL centrifuge tubes
8.1.4 Pyrex beakers
8.1.5 Pyrex or Teflon stirring rods
8.1.6 Stainless steel planchets
8.1.7 Disposable filter funnels

8.2 Instrumentation

8.2.1 Gross Alpha/Beta Proportional Counting System

8.2.2 Gamma Spectrometer and associated electronics and data reduction package

9.0 REAGENTS AND STANDARDS

9.1 Reagents All chemicals should be of reagent grade or equivalent whenever they are commercially available.

9.1.1 Barium carrier (16 mg Ba/mL). Dissolve 30 grams reagent grade $BaCl_2$ x $2H_20$ in 1 L DI water.

9.1.2 50% (w/w) Potassium Carbonate (K_2CO_3)

9.1.3 0.090M Nitric Acid (HNO_3) Dilute 5.5 mL conc HNO_3 to 1000 mL DI water in volumetric flask

9.1.4 0.35 M Nitric Acid (HNO_3) Dilute 11.0 mL conc HNO_3 to 500 mL DI water in volumetric flask

9.1.5 Cerium (500mg/L): Preferably use Ce 500mg/L O2SI standard. Alternatively dissolve 0.155g cerium in 100 mL DI water.

9.1.6 Acetic acid, glacial

9.1.7 1M citric acid. Dissolve 192.13 g citric acid anhydrous powder in 1L DI water

9.1.8 1.5M Ammonium sulfate. Dissolve 200 g ammonium sulfate in 1L DI water

9.1.9 8M Nitric Acid (HNO_3). Add 500 mL conc. HNO_3 (16M HNO_3) to 400 mL DI water, allow to cool, then dilute to 1000 mL with DI water

9.1.10 6M Sodium Hydroxide (NaOH). Cautiously add 120 g NaOH pellets to approximately 300 mL water. When cool, dilute to 500 mL

9.1.11 Sodium Carbonate, 0.75M. Add 79.5g Na_2CO_3 to 1000 mL with DI water

9.1.12 Deionized water (DI water)

9.1.13 pH 10 DI water. Add 6M NaOH dropwise to DI water until a pH of 10 is achieved. Check with pH strip.

9.1.14 Concentrated Hydrofluoric acid (HF)

9.1.15 Concentrated Hydrochloric acid (HCl)

9.1.16 Concentrated Nitric acid (HNO_3)

9.1.17 Concentrated Sulfuric acid (H_2SO_4)

9.2 Standards: Refer to (GL-RAD-M-001) for instructions concerning the preparation of standard solutions.

9.2.1 NIST traceable Ba-133 standard

9.2.2 NIST traceable Ra-228 standard

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Aqueous samples should be collected in plastic bottles and preserved with concentrated Nitric Acid to pH <2.

10.2 Before beginning analysis the analyst must check the sample pH using a pH test strip. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with nitric acid to a pH <2. Once pH is adjusted, the sample must be held in its original container for a minimum of 24 hours before analysis.

11.0 SAMPLE PREPARATION

11.1 Sample Preparation Techniques for Gas Flow Proportional Counting

11.1.1 Measure an appropriate aliquot of water sample into a beaker. Add Barium 133 tracer to all samples and Ra-228 standard to MS and LCS samples. Then add to all samples: 1 mL $BaC1_2$, 10 mL Acetic acid, 5 mL Citric acid, 10 mL Ammonium sulfate. (Record the sample volume and standard spike information on the que sheet.) Allow the sample to settle overnight or until the precipitate settles.

11.1.2 Add Ba-133 tracer (same amount added to samples) to 5 mL of 0.095M nitric solution in a 20mL liquid scintillation vial. This solution will serve as the reference for standard yield determination.

11.1.3 Decant the clear supernate and then transfer the remaining precipitate to a 50 mL centrifuge tube and centrifuge for 5 to 10 minutes at 4000 RPM.

11.1.4 Decant centrifuge tube and remove excess sulfate by washing the precipitate with DI water from a wash bottle.

11.1.5 Centrifuge and decant the DI water wash. Check the pH of the wash solution with a pH strip.

11.1.6 Repeat the washing as necessary until a pH of approximately 6 is observed.

11.1.7 Add 1 mL of 50% potassium carbonate (K_2CO_3) to the precipitate making sure the precipitate is completely submerged in the solution.

11.1.8 Heat in water bath for 4 hours.

11.1.9 Wash the dry slurry with 25 mLs DI water, allow the precipitate to settle, centrifuge and decant the supernate. Check the pH of the wash solution. It should initially be around 12. If a high pH is not observed consult the appropriate group leader or team leader.

11.1.10 Wash the precipitate with 25 mLs of DI water, allow the precipitate to settle, centrifuge and decant. Repeat washings until the pH of the wash solution is approximately 7.

11.1.11 Dissolve the precipitate in 5 mL of 0.095M HNO_3 solution. Centrifuge the solution and decant into a 20 mL scintillation vial. Record date and time of Actinium Ingrowth.

11.1.12 Count the samples and the reference vial from step 11.1.2 on a gamma spectrometer to determine Ba-133 yield. The samples and reference should be given a sample identification number, an identical reference date and counting geometry. Divide the sample result by the reference result to determine the chemical yield.

NOTE: Reference date/time, geometry, and sample volume must be the same for all samples and reference standard in order to perform yield determination by direct comparison.

11.1.13 Allow the sample to ingrow for at least 30 hrs from the time the 5 mL of 0.095 M HNO_3 was added to the centrifuge tubes.

NOTE: The following steps should be performed as rapidly as possible to avoid decay of unsupported Ac-228 with a half-life of 6.13 hours.

11.1.14 Prerinse a LN Spec column with two 5 mL rinses of 0.090 M HNO_3.

11.1.15 Load sample onto the column (record elution time), then add additional 5mL 0.090 M HNO_3. Rinse with additional 12 mL 0.090 M HNO_3 by adding in 3mL increments allowing previous volume to completely drain. Collect the effluent into a labeled centrifuge tube and save in the event reanalysis is required.

11.1.16 Elute the Ac-228 with 10mL of 0.35M HNO_3 into labeled plastic centrifuge tube.

11.1.17 Add 200 µL of 500 ppm Cerium solution to the samples and swirl. Add 2mL of concentrated hydrofluoric acid (HF), swirl and allow to stand for 30 minutes.

11.1.18 Place disposable filter funnel onto filter rig. Check to ensure proper placement of filter in funnel.

11.1.19 Rinse the filter and funnel under vacuum with 80% ethanol. With minimum delay, add the sample to the filtering apparatus and rinse the centrifuge tube several times into the funnel with type II water. Complete the filtering by rinsing the funnel with 80% ethanol after the entire sample has passed through the filter.

11.1.20 Label the bottom side of a 47 mm flat planchet. Place glue on the planchet and carefully place the filter (precipitate side up) on the glue. Care should be taken to make the filter as flat as possible on the planchet.

11.1.21 Count in a gas flow proportional counter for a time duration to meet the contract required detection limit and uncertainty.

11.1.22 If result is above 5 pCi/L, the sample is reeluted on LN spec resin to verify the data. If the result of the reelution is above 5 pCi/L and within 40% of the first result, the second result is reported. If after the reelution the result is not less than 5 pCi/L and not within 40%, the analyst shall consult with the Group Leader or Team Leader.

11.2 Reelution Technique

11.2.1 Count the sample saved in step 11.1.15 on the gamma spectrometer along with a reference that contains the same volume.

11.2.2 Allow the sample to ingrow for at least 30 hours from the time of the last elution. Record the date and time.

11.2.3 Prerinse an Ln Spec column with 10 mL 0.095 M nitric acid (HNO_3).

11.2.3 Load the sample onto the column and record the elution time when the sample is halfway through the column. Add an additional 5 mL 0.090 M HNO_3. Repeat this step for a total of 10 mls. Collect and save the effluent. Proceed to step 11.1.16.

11.3 Re-precipitation technique.

11.3.1 Add 2 drops Thymol blue and add 6 N sodium hydroxide (NaOH) dropwise until sample turns blue.

11.3.2 Add 5 mL 0.75 M sodium carbonate (Na_2CO_3). Microwave for 30 seconds or until precipitation is observed. Allow to cool.

11.3.3 Centrifuge for 5 minutes. Decant supernate.

11.3.4 Continue at step 11.1.11.

11.4 Alternate Procedure for Sample Preparation of Soils and Difficult Matrices

11.4.1 For solid samples, transfer an aliquot to analyze into a Teflon beaker. This aliquot may have previously been muffled in a furnace at approximately 550°C, to reduce interference from organics. Add Ba-133 tracer and Barium carrier ($BaCl_2$). Spike appropriate QC samples with Ra-228 standard.

11.4.2 Digest samples according to procedure GL-RAD-A-015.

11.4.3 Transfer the 5 mL concentrated nitric acid solution to a disposable centrifuge tube. Add an additional 20 mls of conc. nitric acid to the centrifuge tube.

11.4.4 Cap the samples and refrigerate for two hours.

11.4.5 Pull the samples out of the refrigerator and centrifuge for 10 minutes.

11.4.6 Pour off the supernate paying special attention not to pour off any precipitate.

11.4.7 Dissolve precipitate in 25 mls of DI water.

11.4.8 Add 2 drops of phenolphthalein solution. Add 6M NaOH dropwise until the sample turns pink. Add 10 mL of 0.75M Na_2CO_3.

11.4.9 Heat sample in hot water bath for 30 minutes at 90 °C.

11.4.10 Allow the centrifuge tube to cool then centrifuge for 10 minutes.

11.4.11 Pour off the supernate then rinse the precipitate with pH10 DI water. Centrifuge again for 10 minutes and decant.

11.4.12 Dissolve the precipitate completely in 0.090 M $HN0_3$ This may require gentle heating and up to 20 - 35 mls of 0.090 M $HN0_3$. Record date and time of actinium ingrowth. Proceed now to step 11.1.13.

11.4.13 For difficult liquid samples containing a significant amount of sediment, measure an appropriate aliquot into a beaker. Add Barium 133 tracer and Barium carrier ($BaCl_2$) to all samples. Spike appropriate QC samples with Ra-228 standard.

11.4.14 Take samples to dry on a hot plate, then muffle for at least four hours.

11.4.15 Add 10mL of concentrated nitric acid and 10mL of concentrated hydrochloric acid. Reflux for at least three hours.

11.4.16 Take samples to dry. Repeat addition of 10mL of concentrated nitric acid and 10mL of hydrochloric acid. Reflux for 30 minutes or until all solids have leached off the glass.

11.4.17 Transfer leachate to centrifuge tube using 8M nitric acid. Centrifuge and pour liquid into a glass beaker, then take to dry. Transfer pellet into a Teflon beaker using nitric acid.

11.4.18 To liquid portion, add 10mL of concentrated nitric acid and take to dry. Dissolve residue in 10mL of nitric acid.

11.4.19 Digest pellet according to GL-RAD-A-015 until completely digested. Dissolve residue in 10mL of nitric acid and combine with liquid portion.

11.4.20 Transfer sample to a centrifuge tube using 8M nitric acid. Put centrifuge tubes in the freezer for approximately 15 minutes. After samples have cooled, there should be a visible precipitate. Centrifuge and discard supernate.

11.4.21 Add 2mL of concentrated nitric acid and dilute to 30mL with DI water. Add 2-3 drops of phenolthalein indicator, and titrate with 6N sodium hydroxide until the sample turns pink. Add 5 mL of 0.75M sodium carbonate. Digest in hot water bath until precipitate settles. Centrifuge and discard supernate.

11.4.22 Dissolve pellet in 15 mL of concentrated nitric acid and put back in freezer for approximately 15 minutes. Centrifuge and discard supernate.

11.4.23 Repeat step 11.4.21

11.4.24 Dissolve pellet in 5 mL of 0.095M nitric acid. Record date and time of Actinium Ingrowth. Proceed to step 11.1.12.

11.5 Sample Preparation Techniques for Gamma Counting

11.5.1 Measure an appropriate aliquot of water sample into a beaker (s). In each beaker add 10 mL conc. nitric acid, 3 mL BaCL2 carrier, and add appropriate amount of Ba-133 tracer isotope equivalent to Ba-133 value used for calibration. Record the sample volume and standard spike information on the que sheet.

11.5.2 Add 20 mL of concentrated sulfuric acid to samples, stir and allow precipitate to settle to bottom of beaker.

11.5.3 Filter sample through .45 µm Gelman DM-450 or equivalent filters.

11.5.4 Fold filter and place into plastic vial.

11.5.5 Count sample on calibrated gamma spectrometer for appropriate time to meet required MDA.

12.0 QUALITY CONTROL SAMPLES AND REQUIREMENTS

12.1 Refer to (GL-RAD-D-002) for instructions concerning the validation of analysts and analytical methods.

12.2 Method Specific Quality Control Requirements

12.2.1 A method blank should accompany each batch of 20 or fewer samples. The reported value of the blank, should be less than or equal to the contract required detection limit (CRDL).

12.2.2 The Ba-133 tracer added to all samples is used to calculate the method recovery. The method recovery of all samples should be between 25-125% when compared to the reference standard. The method recovery is calculated as follows:

$$\text{Method Recovery} = \frac{Sample(pCi/unit)}{\mathrm{Re}\,f(pCi/unit)}$$

Where:

Sample (pCi/unit) = pCi of Ba-133 reported by gamma spectrometer of the sample.

Ref (pCi/unit) = pCi of Ba-133 reported by gamma Spectrometer of the reference.

12.2.3 A matrix spike (MS) should be run with each batch of 20 or less samples. The recovery of the ms should be between 75-125%. The MS recovery is calculated as follows:

$$\text{MS Recovery(\%)} = \frac{\text{Spike(pCi/unit)} - \text{Sample(pCi/unit)}}{\text{SpikeNominalConcentration(pCi/unit)}} * 100\%$$

Where:

Spike = Results of matrix spike (MS)
Sample = Results of sample that MS was run on Spike Nominal Concentration Spike
Spike Nominal Concentration = Calculated concentration of Ra-228 in the MS solution as follows

$$\text{SNC} = \frac{\text{Ra} - 228\,\text{dpm}}{2.22 * \text{volume in liters}} * \text{ml of spike added}$$

12.2.4 A duplicate sample should be run with each batch of 20 or less samples. The relative percent difference (RPD) between the actual sample and the QC duplicate should be less than or equal to 20% if both the sample and the QC DUP results are greater than 5 times LLD or 100% if either result is less than 5 times LLD. The RPD should be calculated as follows:

$$\text{RPD(\%)} = \frac{\text{HighDup(pCi/unit)} - \text{LowDup(pCi/unit)}}{[(\text{HighDup(pCi/unit)} + \text{LowDup(pCi/unit)}]/2} * 100\%$$

12.2.5 A Laboratory Control Sample (LCS) should be run with each batch of 20 or less samples. The recovery of the LCS should fall between 75-125%. The LCS recovery is calculated as follows:

$$\text{LCS REC(\%)} = \frac{\text{LCSResult(pCi/unit)}}{\text{NominalConcentration of LCS(pCi/unit)}} * 100\%$$

12.3 Actions required if the Quality Control Requirements Are Not Met

If any of the QC criteria from 12.2.1 through 12.2.5 cannot be satisfied, the analyst should inform their group leader and initiate a Nonconformance Report as outlined in "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

NOTE: Client contractual QC requirements override the requirements in this section.

13.0 INSTRUMENT, CALIBRATION, STANDARDIZATION AND PERFORMANCE

13.1 Refer to “Gamma Spectroscopy System Operating Procedures” (GL-RAD-I-001) and to “Operation of the Wallac 1480 Gamma Wizard” (GL-RAD-I-018).

13.2 Refer to “Counting Room Instrumentation Maintenance and Performance Checks” (GL-RAD-I-010) for instructions concerning instrument performance.

13.3 Instrument calibration for Gas Flow Proportional Counters for Ra-228

13.3.1 Prerinse the same number of Tru-Spec columns as detectors that will be calibrated.

13.3.2 Add 5 mL Ra-228 standard in Teflon beaker. Take to dry, and then bring up to 5 mL with 0.5 M HNO_3.

13.3.3 Pre-rinse 5 mLs 0.5 HNO_3. Load sample. Rinse 2 times with 2 mLs 0.5 M HNO_3.

13.3.4 Elute with 15 mLs 3 M HC1.

13.3.5 Proceed to steps 11.1.17 – 11.1.21.

13.3.6 Count each prepared standard in each gas flow proportional detector, ensuring that each detector counts all of the standards at least once.

13.3.7 Determine the detector efficiencies utilizing a calculation spreadsheet according to the following equation:

$$\text{Detector Efficiency} = \frac{\text{Observed cpm - Background cpm}}{\text{Certified dpm}}$$

Where:

Obs cpm = cpm generated by the gas flow proportional counter
Bkg cpm = cpm generated by an unspiked standard blank
Known dpm = dpm decay corrected to the mid point of standard counting

14.0 ANALYSIS AND INSTRUMENT OPERATION

14.1 Refer to “Gamma Spectroscopy System Operating Procedures” (GL-RAD-I-001) or “Operation of the Wallac 1480 Gamma Wizard” (GL-RAD-I-018) for instructions concerning the analysis of the Ba-133 tracer.

14.2 Refer to the appropriate gas flow proportional counting procedure (GL-RAD-I-006) for instructions concerning the analysis of Ac-228.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

15.1 Refer to "Gamma Spectroscopy System Operating Procedures " (GL-RAD-I-001)

15.2 Refer to "Operation of the Wallac 1480 Gamma Wizard" (GL-RAD-I-018).

15.3 Refer to "LB-4100 Gross Alpha/Beta Counter Operating Instructions" (GL-RAD-I-006)

15.4 Refer to "Counting Room Instrumentation Maintenance and Performance Checks" (GL-RAD-I-010).

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

16.1 The analyst will use an Excel spreadsheet, Access, or a client specified formula to calculate the sample Ra-228 pCi/L according to the following equations:

$$\text{Result } (pCi/l) = \frac{(S_{cpm} - B_{cpm}) * A_c}{2.22 * E * V * Y * A_t}$$

16.2 The counting uncertainty for Ra-228 is calculated according to the following equation:

$$\text{Uncertainty (pCi/l)} = \frac{A_c * 1.96\sqrt{((S_{cpm/T_S}) + (B_{cpm}/T_B))}}{2.22 * E * V * Y * A_t}$$

16.3 The method detection limit (MDA) is calculated according to the following equation:

$$\text{MDA (pCi/l)} = \frac{A_c(2.71 + 4.65\sqrt{B_{cpm} * T_s})}{(2.22 * E * V * Y * A_t * T_s)}$$

Where:

T_B=Amount of time background was counted (min)
T_S=Amount of time sample was counted (min)
S_{cpm}=Sample counts per minute
B_{cpm}= background counts per minute
E=efficiency
V=sample volume (liters)
t=time in minutes from separation to counting
A_t=Ac-228 decay correction(A_t) = $e^{-0.00188*t}$
A_c=count duration decay correction (A_c)=Ts*.00188/(1- $e^{-0.00188*Tc}$)
Y= yield

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

Data is reviewed and packaged in accordance with GL-RAD-D-003 for Data Review, Validation, and Data Package Assembly.

18.0 RECORDS MANAGEMENT

Records generated as a result of this procedure are maintained as quality documents in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

19.0 LABORATORY WASTE HANDLING AND DISPOSAL

Laboratory waste is disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.0 REFERENCES

20.1 "Radiochemical Analytical Procedures for Analysis of Environmental Samples." March 1979. EPA EMSL.

20.2 "Radiochemistry Procedures Manual." EPA 520/5-84-006, December 1987, Method Ra-05.

20.3 "Prescribed Procedures for Measurement of Radioactivity in Drinking Water." EPA 600/4-80-032, August 1980, Method 904.0.

20.4 "Test Methods for Evaluating Solid Waste," US EPA, June 1997, SW-846.

20.5 Special thanks to Dr Bill Burnett and his associates for their development of this method at Florida State University.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE ISOTOPIC DETERMINATION OF AMERICIUM, CURIUM, PLUTONIUM AND URANIUM

(GL-RAD-A-011-REVISION 14)

APPLICABLE TO METHODS:
DOE RP800 1997 (Modified)
EML HASL-300 U-04-RC (Modified)

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1.0 STANDARD OPERATING PROCEDURE FOR THE ISOTOPIC DETERMINATION OF AMERICIUM, CURIUM, PLUTONIUM, AND URANIUM.

2.0 METHOD OBJECTIVE, PURPOSE, CODE, AND SUMMARY

2.1 This standard operating procedure provides the necessary instructions to conduct the analysis for isotopic americium, curium, plutonium and uranium in a variety of liquid and solid matrices. This method also gives specific guidance on determining U-232 and Am-243, which are typically used as isotopic tracers.

2.2 A sample is digested, if necessary, and aliquoted. Transuranic elements are scavenged by coprecipitation with iron hydroxide. The precipitate is dissolved and separation of elements is accomplished through extraction chromatography and ion exchange resins. The elements are then prepared for the measurement of radioactive isotopes by coprecipitation with Neodymium fluoride. The Neodymium fluoride precipitate is trapped on a filter, mounted on a stainless steel disk and placed in a partially evacuated chamber for measurement of isotopic alpha emission.

2.3 This method has been modified from the source method from EML Methods Manual HASL 300 U-04-RC and uses similar principles of radiochemical separation and counting. This method is also very similar in concept to the source method from the DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800, “Sequential Separation of Americium and Plutonium by Extraction Chromatography.”

2.4 This method has been modified on the basis of GEL’s Performance Based Measurement System (PBMS).

3.0 METHOD APPLICABILITY

3.1 Method Detection Limit: Typical minimum detectable activity (MDA) for samples analyzed for U/Am/Cm/Pu is 1 pCi/L or 0.1 pCi/g for all isotopes.

3.2 Method Precision: Typical relative percent difference (RPD) is 20%.

3.3 Method Bias (Accuracy): Acceptable criteria for method accuracy, measured by running with each batch a laboratory control sample, is ±25% of true value.

3.4 Analysts are trained and certified to perform this analysis after the analyst has completed a batch with acceptable duplicate and laboratory control sample, as well as completed an unknown sample within ±25% of true value. Analyst training records are maintained in accordance with GL-QS-E-008 and kept on hand in the Quality Control Department.

4.0 DEFINITIONS

4.1 National Institute of Standards and Technology (NIST). For the purpose of this method, the national scientific body responsible for the standardization and acceptability of analyte solutions.

4.2 Type II water: Deionized water.

4.3 ALPHALIMS: Laboratory Information Management System.

5.0 METHOD VARIATIONS

Some variations may be necessary due to special matrices encountered in the lab. These variations may be used with approval from a Group or Team Leader. Variations to a method will be documented with the analytical raw data.

6.0 SAFETY PRECAUTIONS AND WARNINGS

6.1 Personnel performing this analytical procedure are trained in and follow the safe laboratory practices outlined in the Safety, Health and Chemical Hygiene Plan, GL-LB-N-001.

6.2 Personnel handling radioactive materials are trained in and follow the procedures outlined in GL-RAD-S-004 for Radioactive Material Handling.

6.3 Personnel handling biological materials are trained in and follow the procedures outlined in GL-RAD-S-010 for Handling Biological Materials.

6.4 If there is any question regarding the safety of any laboratory practice, **stop immediately**, and consult qualified senior personnel such as a Group or Team Leader.

7.0 INTERFERENCES

7.1 Internal tracer standards may have ingrown daughters that may interfere with the analysis. For example Th-228 will be present in aged U-232 standard, Fr-221 will be present in Th-229, which will interfere with the curium analysis, and U-232 will be present in Pu-236. These problems are overcome by running separate aliquots of sample for thorium analysis.

7.2 Short lived radioactive progeny may ingrow on prepared filters. For example, the Ra-224 alpha peak will be present if the Th-228 parent is present. These interferences are minimized by counting ssample as soon as possible after separation chemistry.

8.0 APPRATUS, MATRIALS, REAGENTS, EQUIPMENT AND INSTRUMENTATION

8.1 Ancillary Equipment

8.1.1 Silicon surface barrier detectors with associated electronics, vacuum chambers, and data reduction capabilities

8.1.2 Eichrom Technologies TEVA Resin, 100 – 150 µ particle size

8.1.3 Eichrom Technologies TRU Resin, 100 – 150 µ particle size

8.1.4 Vacuum pump and filtration apparatus

8.1.5 8.1.5 Disposable filter funnels (containing 25 mm polypropylene filters with 0.1 µm pore size)

8.1.6 Stainless steel disks. 29 mm diameter

8.1.7 Stainless steel tweezers

8.1.8 Polypropylene centrifuge tube (50 mL)

8.1.9 Sample drying and ashing apparatus

8.1.10 Sample homogenization apparatus

8.2 Reagents, Chemicals and Standards

8.2.1 Neodymium chloride (500 mg/L)

8.2.2 Neodymium chloride (10,000 mg/L)

8.2.3 Carbon Colorant. Place four47mm cellulose nitrate filters in a beaker and add 5mL concentrated H_2SO_4. Cover and heat on a hot plate with medium-high heat for 2-4 hours. Cool completely. Slurry the residue in DI water and dilute to 1 L with DI water.

8.2.4 Hydrochloric acid (9 M): Dilute 750 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.5 Hydrochloric acid (4 M): Dilute 333 mL of concentrated hydrochloric acid to 1 L with DI water.

8.2.6 Hydrochloric acid concentrated (12 M)

8.2.7 9 M hydrochloric acid/0.05 M ammonium iodide. Dissolve 7.24 g of ammonium iodide in 750 mL of concentrated HCL and dilute to 1 L with DI water. PREP DAILY.

8.2.8 Hydrochloric acid (6 M). Dilute 500 mL of concentrated hydrochloric acid to 1 L with DI Water.

8.2.9 6 M hydrochloric acid/0.52 M Hydrofluoric acid. Dilute 500 mL of concentrated hydrochloric acid and 18.6 mL of 49% hydrofluoric acid to 1 L DI water.

8.2.10 25% Hydrazine dihydrochloride. Dissolve 25 g of hydrazine dihydrochloride in 75 mL of DI water and dilute to 100 mL with DI water.

8.2.11 9 M Hydrochloric acid/0.04% Hydrogen peroxide. Add 8 drops of 30% hydrogen peroxide to 1 L of 9 M HCL. PREP DAILY.

8.2.12 Ethyl alcohol (80%). Dilute 800 mL ethanol to 1 L with DI water.

8.2.13 Hydrochloric acid 0.1M. Dilute 8.3 mL of concentrated HCL to 1 liter with DI water.

8.2.14 Hydrofluoric acid concentrated (49%)

8.2.15 Hydrogen peroxide (30%)

8.2.16 Ion exchange resin. AG 1X8, chloride form, 100-200 mesh

8.2.17 Iron Carrier (10 mg/mL). Dissolve 62.7 g of $Fe(NO_3)_3 \bullet 6H_2O$ or 72.3 g of $Fe(NO_3)_3 \bullet 9H_2O$ in 800 mL DI water and dilute to 1 Liter with DI water.

8.2.18 NIST traceable standards: U-232, Am-241, Am-243, Cm-244, U-238, Pu-242, Pu-239, Pu-238, Pu-236

8.2.19 Nitric acid concentrated (16M)

8.2.20 Nitric acid (2M). Dilute 125mL of concentrated nitric acid to 1 L with DI water.

8.2.21 Nitric Acid (1M). Dilute 62.5 mL concentrated nitric acid to 1 L with DI water

8.2.22 2M Nitric Acid/1M Aluminum Nitrate. Dissolve 375.13g of aluminum nitrate in 127.3 mL of concentrated nitric acid and dilute in 1 L with DI water.

8.2.23 Titanium (III) Chloride. 20% reagent

8.2.24 10 M Hydrochloric acid. 835mL of concentrated hydrochloric acid diluted to 1 L with DI water.

8.2.25 2 M Hydrochloric acid. 167 mL of concentrated hydrochloric acid diluted to 1 L with DI water

8.2.26 1 M Nitric acid. 62.5 mL of concentrated nitric acid diluted to 1 L with DI water.

8.2.27 1.25 M Calcium nitrate. Dissolve 204 g of Calcium nitrate in 500 mL of DI water and dilute to 1 L with DI water.

8.2.28 Phosphoric acid concentrated.

8.2.29 Lanthanum (10,000 mg/L)

8.2.30 10% Sulfuric acid. 10 mL of concentrated sulfuric acid diluted to 100 mL with DI water.

8.2.31 Formic acid (concentrated).

8.2.32 4 M Ammonium thiocyanate/0.1 M Formic acid. Add 60 g of Ammonium thiocyanate and 1.0 mL of concentrated Formic acid to a graduated cylinder and dilute to 200 mL with DI water. Prepare fresh daily.

8.2.33 1.5 M Ammonium thiocyanate/0.1 M Formic acid. Add 9.5 g of Ammonium thiocyanate and 0.5 mL of concentrated Formic acid to a graduated cylinder and dilute to 100 mL with DI water. Prepare fresh daily.

8.2.34 Substrate Suspension: Dilute 4 mL of neodymium chloride (10,000 mg/L), 80 mL of [HCl] and 40 mL of carbon suspension to 1500 mL with Deionized water. Add, and while swirling, 40 mL [HF] and dilute to 2L with Deionized water.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples should be preserved to approximately pH 2 with nitric acid and collected in a plastic bottle.

9.2 Before beginning an analysis the analyst should check the sample pH with a pH strip. If the sample is received with a pH greater than 2, the analyst should contact the Group Leader or Team Leader. If approved by the client, the analyst should adjust the pH with Nitric Acid to a pH=1-2. If the sample is pH adjusted, let the sample sit in the original container for a minimum of 24 hours before analysis.

9.3 If the sample has exceeded the hold time the analyst should contact the Group Leader before continuing with the batch.

9.4 Soil samples require no preservation and may be shipped in any suitable container.

10.0 SAMPLE PREPARATION

Soil Sample Preparation:

10.1 If not already done, homogenize the sample by performing "Soil Sample Preparation for the Determination of Radionuclides" (GL-RAD-A-021).

10.2 It is recommended that the samples be ashed in a muffle furnace as specified in "Soil Sample Ashing for the Determination of Radionuclides" (GL-RAD-A-021B).

10.3 For uranium analysis, take an appropriate aliquot and digest as specified in GL-RAD-A-015.

10.4 A separate Am/Cm/Pu aliquot is treated with an aggressive acid leach as described in the following steps. Uranium should not be run by this leaching technique.

10.4.1 Place the sample in a beaker and add 10 mL of concentrated HCl and 10 mL of concentrated HNO_3 per gram of sample with a minimum of 10 mL. Add the appropriate tracers as described in section 10.5.

10.4.2 If necessary, add 1 mL of iron carrier (10mg/mL).

10.4.3 Heat the samples and cover with a watch glass. Allow to leach for a minimum of 2 hours. Agitate the sample periodically to enhance the leaching process.

10.4.4 Allow the sample to partially cool and transfer to a centrifuge tube. Centrifuge to separate the solid and leached portions of the sample.

10.4.5 Decant the leachate to a clean labeled beaker and rinse the solid phase with DI water. Centrifuge the sample and decant the leachate into the beaker.

10.4.6 Evaporate the solution to dryness.

10.4.7 Add 5 to 10 mL of concentrated HCl to the beaker and evaporate to dryness.

10.4.8 Proceed to step 10.9.

<u>Aqueous Sample Preparation:</u>

10.5 Add an appropriate aliquot of sample to a labeled beaker. Add a certified dpm of the following tracers to each of the samples:

10.5.1 For isotopic uranium, U-232 is normally used

10.5.2 For isotopic americium and curium, Am-243 is used

10.5.3 For isotopic plutonium, Pu-242 is normally used

10.5.4 If the analysis of the sample calls for quantification of U-232 or Am-243, the following steps shall be taken:

10.5.5 The sample will be run normally with the tracer indicated in 10.5.

10.5.6 Review of the data shall be undertaken to determine if there are any peaks in the spectrum with which a ratio can be setup with the tracer isotope.

10.5.7 If there is a peak with which a ratio can be setup, then a second run of the sample shall completed with no tracer addition, and the ratios of peaks used to make corrections as described in the equations in section 15.4.

10.5.8 If no suitable peaks are available to ratio, a second run of the sample shall be made with a different tracer isotope such as U-236 or Cm-244. The quantification of the isotope that was normally the tracer can then be made. If there is any quantifiable activity a correction can be made to the initial run by calculating a correction ratio for the tracer recovery of the first run from the second run results and following the equations outlined in 15.5.

NOTE: Other sample matrices, such as vegetation, air filters, tissue etc. are run as outlined in "Preparation of Special Matrices for the Determination of Radionuclides" (GL-RAD-A-026). The analyst must ensure that the appropriate tracer(s) are added to these other matrices as discussed in section 10.5.1.1-10.5.1.4.

10.6 Add 1 mL of iron carrier (10 mg/mL).

10.7 Bring to a slight boil and add concentrated NH_4OH until turbidity persists, or pH>9. Heat to boiling for 10 minutes and then allow to settle and cool.

10.8 Decant excess supernate and discard. Collect the remaining precipitate by centrifugation in a 50 mL centrifuge tube and discard the supernate.

NOTE: Exercise care in this step because finely divided material that contains the actinides may also be present in addition to the large iron hydroxide flocks.

10.9 Dissolve the precipitate or residue from step 10.4.8 in 10-15 mL of 9M HCl/0.04% H_2O_2 solution.

NOTE: Samples may be dissolved with 10 to 15 mL of 9M HCl and then add 1 drop of 30% H_2O_2 as an alternative to dissolving with 9M HCl/0.04% H_2O_2.
NOTE: If U only is required the load solution is 10 – 15 mL of 9 M HCl.

10.10 Slurry AG 1x8 anion resin (Cl form 100-200 Mesh) in a squirt bottle with DI water. Transfer the resin to a small column to obtain a settled resin bed of 2.5 mL.

10.11 Condition the column with 10 mL of 9 M HCl.

10.12 Pass the sample solution from step 10.9 through the column and catch the effluent in a labeled, disposable 50 mL centrifuge tube for americium/curium analysis.

10.13 Rinse the column with 5 mL of 9 M HCl and catch with the Am/Cm fraction. Proceed to step 10.19 for Am/Cm analysis. See note prior to step 10.19.

10.14 Rinse the column with an additional 15 mL of 9 M HCl and catch in a drip pan for disposal.

10.15 Elute plutonium by adding 15 mL of 9M HCl/0.05 NH_4I solution, catching the Pu elute in a labeled, disposable 50 mL centrifuge tube. Proceed to step 10.41 for plutonium cookdown and microprecipitation for alpha spectroscopy.

10.16 Rinse the column with 15 mL of 6M HCl/0.52 M HF and catch in a drip pan for disposal.

10.17 Rinse the column with 5 mL 6M HCl and catch in a drip pan for disposal.

10.18 Elute uranium from the column by adding 15mL of 0.1M HCl, catching the uranium elute in a labeled, disposable 50mL centrifuge tube.

10.18.1 Transfer sample to a clean beaker with DI water and evaporate to dryness over low heat.

10.18.2 Dissolve sample with 4mL of 2M HCl. Transfer to a clean centrifuge tube with DI water.

10.18.3 Proceed to step 10.43for uranium microprecipitation for alpha spectroscopy.

Am Separation via TRU Resin:

NOTE: If sample aliquot is small or liquid sample is clean and free of particulates continue with step 10.19 and TRU column work. If not, proceed to step 10.23 for additional clean-up steps and TRU column work.

10.19 Precondition a 2 mL TRU column with 5 mL of 9M HCl.

10.20 Pass the sample solution from step 10.13 through the column catching in a drip pan for disposal.

10.21 Rinse the column with 5 mL of 9M HCl catching in a drip pan for disposal.

10.22 Elute Americium and Curium with 20 mL of 4M HCl catching in a clean, labeled, disposable centrifuge tube. Proceed to step 10.36.

10.23 Add 0.5 mL of 1.25 M Calcium nitrate to the elution from step 10.13.

10.24 Add 1.0 mL of Phosphoric acid. Swirl to mix.

10.25 Dilute to 30 mL with DI water.

10.26 Add concentrated Ammonium hydroxide to pH of 8 to 10 to precipitate Calcium phosphate. Do not over precipitate.

10.27 Spin samples in a centrifuge and pour off supernate.

10.28 Add 25 mL of DI water to centrifuge tube, cap, and shake vigorously to break up precipitate.

10.29 Spin samples in a centrifuge and pour off supernate.

10.30 Add 15 mL of 2 M Nitric acid/1 M Aluminum nitrate to centrifuge tube and dissolve precipitate. Gently heat if necessary. Solution should be clear.

10.31 Precondition a 2 mL TRU spec NO PRERESIN column with 10 mL of 2 M Nitric acid, catching the rinse in a drip pan for disposal.

10.32 Pass the sample solution from step 10.30through the column, catching the load solution in a drip pan for disposal.

10.33 Rinse the column twice with 5 mL of 2 M Nitric acid and catch the rinse in a drip pan for disposal.

10.34 Rinse the column with 5 mL of 1 M Nitric acid and catch the rinse in a drip pan for disposal.

10.35 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute Am and Cm from the column using 2 mL of 10 M Hydrochloric acid, followed by 10 mL of 4 M Hydrochloric acid.

10.36 If rare earth elements are suspected in sample proceed to Step 10.53 to separate rare earth elements via TEVA resin, otherwise, continue with Step10.37.

Americium Cookdown:

10.37 Transfer the Am/Cm elution to a clean beaker. Add 4 drops of Fe carrier and gently cook dry.

10.38 Add 10 mL of concentrated Nitric acid and 2 mL of 30% Hydrogen peroxide, cover and reflux until evolution of gas bubbles ceases. Remove the cover and gently cook dry.

10.39 Dissolve the residue in 4 mL of 2 M Hydrochloric acid with gentle heating for 5 to 10 minutes. If residue does not dissolve repeat Step10.38. Cool and transfer to a clean disposable centrifuge tube using 1 to 2 mL of DI water to rinse the beaker.

10.40 Add 0.1 mL of Neodymium carrier (500 mg/L) to the solution and swirl to mix. Add 2 mL of concentrated Hydrofluoric acid and swirl to precipitate fluorides. Allow solution to sit for 30 minutes then proceed to Step 10.44.

Plutonium Cookdown and Microprecipitation:

10.41 Transfer the plutonium solution from step 10.15 to a clean beaker. Add 4 drops of iron carrier (10 mg/mL) and 10 mL of concentrated nitric acid. Evaporate the solution to dryness on medium to low heat. Dissolve the residue with 4 mL of 2 M hydrochloric acid. Use DI water to transfer the solution to a centrifuge tube.

10.42 Add 0.1 mL of Neodymium carrier (500 mg/L) and swirl. Add 3 to 4 drops of 25% Hydrazine dihydrochloride and swirl to mix. Let the solution sit for 10 minutes, then add 2 mL of 49% Hydrofluoric acid. Swirl to mix. Allow to sit for 30 minutes, then proceed to step 10.44.

Uranium Microprecipitation:

10.43 To the uranium solution from step 10.18, add 1 mL of titanium trichloride solution and allow the sample to sit for 30 seconds. Add 0.1 mL of Neodymium carrier solution (500 mg/L) and swirl to mix. Add 2 mL of concentrated hydrofluoric acid to precipitate fluorides. Allow the solution to sit for 30 minutes, then proceed to step 10.44.

Sample Filtration:

10.44 Place a disposable filter funnel on the filter support screen. Wet the filter with 80% ethyl alcohol and apply vacuum.

10.45 Rinse the funnel with 80% ethyl alcohol.

10.46 Add 5 mL of substrate suspension. After solution has passed through filter, add another 5 mL of substrate suspension.

10.47 Add 1 mL of the carbon colorant.

10.48 Filter the fluoride precipitated solution through the filter paper. Rinse the centrifuge tube with ≈ 5 mL DI water and pass through filter.

10.49 Rinse the funnel with 80% ethyl alcohol.

Caution – Directing a stream of liquid onto the filter will disturb the distribution of the precipitate on the filter and render the sample unsuitable for alpha spectrometry resolution.

10.50 Without turning off the vacuum, remove the funnel.

10.51 Turn off vacuum and remove filter. Mount filter on a labeled 29mm flat planchet. Ensure that the filter is centered and as flat as possible on the planchet.

NOTE: Care should be taken not to touch the active area of the filter with tweezers.

10.52 Place the mounted filter under a heat lamp for 5 minutes prior to alpha spectrometry measurement.

10.53 Count under vacuum on the alpha spectrometer long enough to reach requested MDA. Consult the operating manual for instruction on operating the alpha spectrometer.

Separation of Am from the Rare Earth Elements via TEVA Resin:

10.54 Transfer the elution from Step 10.31 to a clean beaker and add 0.3 mL of Lanthanum. Gently cook dry.

10.55 Once the samples have cooled, add 5 mL of concentrated Nitric acid and 2 mL of 30% Hydrogen peroxide. Heat on a hot plate at low heat (with a cover in place) to complete to dryness. Cool and repeat.

10.56 Dissolve residue in 3 drops of 10% Sulfuric acid. Evaporate until a very small amount of acid remains.

10.57 Dissolve residue in 3 drops of concentrated Formic acid. Evaporate until a very small amount of acid remains.

10.58 Repeat Step 10.56and evaporate the sample under low heat until the beaker is gently dry.

10.59 Dissolve the sample in 10 mL of 4 M Ammonium Thiocyanate/0.1 M Formic acid. Be sure that the 4 M Ammonium Thiocyanate/0.1 M Formic acid is prepared fresh daily.

10.60 Condition a TEVA column with 5 mL of 4 M Ammonium Thiocyanate/0.1 M Formic acid, catching the rinse in a drip pan for disposal.

10.61 Load the sample onto the TEVA column, catching the load in a drip pan for disposal.

10.62 Rinse the beaker with 5 mL of 4 M Ammonium Thiocyanate/0.1 M Formic acid and add to the column, catching the rinse in a drip pan for disposal.

10.63 Rinse Lanthanum and other rare earth elements from the column with 10 mL of 1.5 M Ammonium Thiocyanate/0.1 Formic acid, catching the rinse in a drip pan for disposal. Be sure that the 1.5 M Ammonium Thiocyanate/0.1 Formic acid is prepared fresh daily.

10.64 Place a labeled, disposable 50 mL centrifuge tube under each column. Elute Am with 20 mL of 2 M Hydrochloric acid.

10.65 Proceed to Step 10.40 to precipitate and filter samples.

11.0 Preparation of Standard Solutions and Quality Control Standards

Refer to "Preparation and Verification of Radioactive Standards" (GL-RAD-M-001).

12.0 Instrument Calibration and Performance

For direction on calibration and instrument performance see "The Alpha Spectroscopy System" (GL-RAD-I-009).

13.0 Analysis and Instrument Operation

For analysis and instrument operation see "The Alpha Spectroscopy System" (GL-RAD-I-009).

14.0 Equipment and Instrument Maintenance

For maintenance of system see "Counting Room Instrumentation Maintenance and Performance Checks" (GL-RAD-I-010).

15.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

15.1 The instrument will report sample pCi/unit according to the following equation:

$$\text{Result (pCi/unit)} = \frac{S_{cpm} - B_{cpm}}{2.22 * E * V * A * \text{decay} * R}$$

15.2 Counting uncertainty is propagated according to the following equation:

$$\text{Uncertainty (pCi/unit)} = Ac * 1.96\sqrt{\left(\frac{ef\_er}{E}\right)^2 \left(\frac{pk\_er}{pk}\right)^2 \left(\frac{ab\_er}{A}\right)^2 + \left(\frac{sy}{100}\right)^2 + (dk)^2}$$

15.3 The minimum detectable activity (MDA) is calculated according to the following equation:

$$\text{MDA(pCi / unit)} = \frac{2.71 + 4.65 * \sqrt{B_{cpm} * T_c}}{(2.22 * E * V * R * A * \text{decay} * T_c)}$$

Where:

$$e\left(\frac{-\ln(2)T_d}{T_{1/2}}\right)$$

$$R = \frac{T_{cpm} - B_{cpm}}{T_{dpm} * E}$$

$$dk = \frac{T_{1/2}err}{T_{1/2}} * \left(\frac{\lambda Tr}{1 - e^{-\lambda Tr}} - \lambda\left(T_c + T_r\right) - 1\right)$$

And where:

Scpm	=	Sample counts per minute
Bcpm	=	Background counts per minute
E	=	Counting efficiency (decimal form)
V	=	Volume in liters,g,cfm, etc.
A	=	Isotopic abundance (decimal form)
ef_er	=	1 sigma efficiency error (decimal form)
pk_er	=	1 sigma peak error
ab_er	=	1 sigma isotopic abundance error (decimal form)
sy	=	1 sigma systematic error
pk	=	Peak area
R		Tracer recovery
Tc	=	Sample count time in minutes
Td	=	Time interval for radioactive decay
Tr	=	Elapsed real time in minutes
Tcpm	=	Tracer counts per minute
Tdpm	=	Tracer known disintegrations per minute

Ac	=	Sample calculated activity
T1/2	=	Isotopic half life
T1/2err	=	Isotopic half life error
λ	=	Isotopic decay constant
e	=	exponential function
ln	=	natural log function

15.4 This section describes the calculation of U-232 by a ratio method. This process uses two analyses of the same sample, one run traced with U-232 and one run untraced. A limitation of this method is that sufficient activity of a non-tracer isotope (such as U-238) must be present to ratio the two peaks. Because of this limitation, the preferred method is to use a two-tracer approach as described in 15.5.

15.4.1 Ratio determination: To set up a ratio between the peaks of the untraced sample run, use the following equation.

$$\text{Ratio} = \frac{U_{232u}}{U_{238u}}$$

15.4.2 The corrected yield of the U-232 traced sample is calculated as follows:

$$U_{232s} = U_{238i} * \text{Ratio}$$
$$U_{232t} = U_{232i} - U_{232s}$$

$$\text{Yield}_{\text{corrected}} = \frac{U_{232t}}{E * T_{dpm} * T_c}$$

Where:

U232s	=	U-232 counts in the traced sample run due to sample activity.
U238i	=	total U-238 counts in the traced sample run
U232i	=	total U-232 counts in the traced sample run
U232t	=	U-232 counts in the traced sample run due to the tracer addition
U232u	=	U-232 counts in the untraced sample run
U238u	=	U-238 counts in the untraced sample run
E	=	Efficiency for the detector used in analysis
Tdpm	=	Known dpm of the U-232 tracer added
Tc	=	Time interval of the sample count in minutes

15.4.3 The final results are then corrected by substituting the corrected yield into the equations listed in sections 15.1 through 15.3.

15.5 This section describes the calculation of U-232 by an alternate tracer method. This process uses two analyses of the same sample, one run traced with U-232 and one run traced with U-236 (or another suitable standard).

NOTE: No corrections are necessary, if there is no U-232 activity in the U-236 traced run. If U-232 activity is present in the U-236 traced run, then the yield of the U-232 must be corrected as follows:

$$U_{232s} = U_{232f} * \left(\frac{eff_i}{eff_f}\right) * \left(\frac{counttime_i}{counttime_f}\right) * \left(\frac{squant_i}{squant_f}\right)$$

$$U_{232t} = U_{232obs} - U_{232s}$$

$$Yield_{corr} = \frac{U_{232t}}{\left(Eff_i * Counttime_i * U_{232tadded}\right)}$$

Where:

U232s	=	U-232 counts in the traced sample run due to sample activity.
U232t	=	U-232 counts in U-232 traced analysis due to tracer addition
U232f	=	U-232 counts in the U-236 traced analysis
U232added	=	U-232 dpm added as the tracer
U-232obs	=	Total U-232 counts observed in the U-232 traced analysis
Effi	=	Efficiency of detector used in U-232 traced analysis
Eff_f	=	Efficiency of detector used in U-236 traced analysis
$Counttime_i$	=	Count time of U-232 traced analysis
$Counttime_f$	=	Count time of U-236 traced analysis
$Squant_i$	=	Sample aliquot of U-232 traced analysis
$Squant_f$	=	Sample aliquot of U-236 traced analysis
$Yield_{corr}$	=	Corrected Yield of U-232 traced analysis

15.5.1 The final results are then corrected by substituting the corrected yield into the equations listed in sections 15.1 through 15.3:

15.6 Record the following information on the alpha que sheet: preparation date, analyst's initials, spike isotope, spike code, spike volume, LCS isotope, LCS code, LCS volume. For each sample record the detector number, sample mass, sample date, and sample time.

16.0 QUALITY CONTROL REQUIREMENTS

16.1 Analyst and Method Verification

16.1.1 Refer to "Analytical Methods Validation for Radiochemistry" (GL-RAD-D-002) for instructions concerning the validation of analysts and analytical methods.

16.2 Method Specific Quality Control Requirements

16.2.1 A method blank will accompany each batch of 20 or less samples. The reported value should be less than or equal to the CRDL for all target isotopes.

16.2.2 A matrix spike (MS) should be run with every batch of 20 or less samples. The recovery of the spike should fall between 75 and 125%. If the sample activity is 5 times the MS nominal concentration, no limits are applied. The recovery is calculated as follows:

$$\%Rec = \frac{spike(pCi/unit) - sample(pCi/unit)}{spikedamount(pCi/unit)} * 100$$

16.2.3 A sample duplicate should be run with every batch of 20 or less samples. The relative percent difference (RPD) between the sample and the duplicate should be less than or equal to 20%. The RPD is calculated as follows.

$$RPD = \frac{\text{high sample}(pCi/unit) - \text{low sample}(pCi/unit)}{\text{Average }(pCi/unit)} * 100$$

16.2.4 A laboratory control spike (LCS) should be run with every batch of 20 samples or less. The recovery of the spike should fall between 75 and 125%. The recovery is calculated as follows:

$$LCS = \frac{observed\_pCi/unit}{known\_pCi/unit} * 100$$

16.3 Actions required if the Quality Control Requirements are not met

16.3.1 If any of the above criteria cannot be satisfied, the analyst should inform the Group Leader and initiate a non-conformance report as outlined in "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

17.0 Data Review, Approval, and Transmittal

Refer to "Data Review, Validation and Data Package Assembly" (GL-RAD-D-003) for instructions concerning the data review process, approval, and transmittal.

18.0 Records Management

18.1 Each analysis that is performed on the instrument is documented in the run log according to “Run Logs” (GL-LB-E-009).

18.2 All raw data printouts, calculation spreadsheets and batch checklists are filed with the sample data for archival and review.

19.0 Laboratory Waste Handling And Waste Disposal

Radioactive samples and material shall be handled and disposed of as outlined in the Laboratory Waste Management Plan (GL-LB-G-001).

20.0 References

20.1 EPA Environmental Monitoring and Support Laboratory. Las Vegas. Radiochemical Analytical Procedures for Analysis of Environmental Samples. March 1979.

20.1 EML Procedures Manual HASL-300, 1982, Method U-04-RC.

20.2 DOE Methods Manual for Evaluating Environmental and Waste Management Samples, 1997 Edition, RP800, “Sequential Separation of Americium and Plutonium by Extraction Chromatography.”

20.3 Analytical Chemistry. Rapid Determination of Th-230 in Mill Tailings by alpha spectroscopy. UNC Geotech, Grand Junction Projects Office. Steve Donivan, Mark Hollenbach, and Mary Costello. Vol. 59, No. 21, 1987.

20.4 Los Alamos Health and Environmental Chemistry: Analytical Techniques. LA-10300-M Vol. 1, September 1987.

20.5 Special thanks to Dr. Bill Burnett and his associates for assistance in developing this method at Florida State University.

APPENDIX 1

AMERICIUM, CURIUM, PLUTONIUM, AND URANIUM

Use a 2.5 cm^3 column with 1X8 anion resin (Cl^- form 100-200 mesh)

COLUMN WORK

____ 10 mL 9M HCl (Conditioning)

____ Load solution: 10 – 15mL 9M HCl / 0.04% H_2O_2 (Catch in C-Tube for Am/Cm)
NOTE: If U only is required the load solution is 10 – 15 mL of 9 M HCl

____ 5mL 9M HCl (Catch in C-Tube for Am/Cm then proceed to Appendix 2 or 3 as approriate for Am/Cm procedure)

____ 15mL 9M HCl (Rinse)

____ **Elute** Pu: 15mL 9M HCl / 0.05M NH_4I (Catch in C-Tube then proceed to Appendix 4 Plutonium Cook-down)

____ 15mL 6M HCl / 0.52 M HF (Rinse)

____ 5mL 6M HCl (Rinse)

____ **Elute** U: 15mL 0.1M HCl (Catch in C-Tube)

____ Transfer to a clean beaker and evaporate to dryness

____ Dissolve with 4mL of 2M HCl and transfer to centrifuge tube with DI water.

____ Proceed to Appendix 4 for Uranium Precipitation

PLUTONIUM COOK-DOWN

____ Transfer to a clean beaker. Add 4-6 drops of Fe carrier, 10mL of [HNO_3], and evaporate the solution to dryness on medium heat.

____ Dissolve with 4mL of 2M HCl and transfer to centrifuge tube with DI water.

____ Proceed to Appendix 4 for Plutonium Precipitation

APPENDIX 2

AMERICIUM / CURIUM CONTINUATION

AMERICIUM / CURIUM

____ 0.5 mL 1.25 M Calcium nitrate

____ 1.0 mL Phosphoric acid and swirl

____ Dilute to 30 mL with DI water

____ [NH_4OH] to pH of 8 to 10

____ Centrifuge samples and pour off supernate

____ 25 mL DI water and shake samples to break up precipitate

____ Centrifuge samples and pour off supernate

____ 10 mL 2 M HNO_3 (Condition 2 mL TRU Resin Column)

____ Load Solution: 15 mL 2 M HNO_3 / 1 M $Al(NO_3)_3$

____ 5 mL 2 M HNO_3 (Rinse)

____ 5 mL 2 M HNO_3 (Rinse)

____ 5 mL 1 M HNO_3 (Rinse)

____ **Elute** Am/Cm: 2 mL 10 M HCl (Catch in C-Tube)

____ **Elute** Am/Cm: 10 mL 4 M HCl (Catch in C-Tube)

____ Transfer to a clean beaker. Add 4-6 drops of Fe carrier, and gently cook dry

____ 10 mL [HNO_3] and 2 mL 30% H_2O_2, reflux, then gently cook dry

____ Dissolve with 4 mL of 2 M HCl and transfer to centrifuge tube with DI water

____ Proceed to Appendix 4 for Am/Cm precipitation

APPENDIX 3

AMERICIUM / CURIUM CONTINUATION

AMERICIUM / CURIUM

___ 5 mL 9M HCl (Conditioning)

___ Load solution from Appendix 1 (catch in drip pan)

___ 5mL 9M HCl (Rinse)

___ **Elute** Am/Cm: 20 mL 4M HCl (Catch in C-tube)

___ Transfer to a clean beaker. Add4-6 drops of Fe carrier, and gently cook dry.

___ 10 mL [HNO3] and 2 mL 30%, reflux, then gently cook dry

___ Dissolve with 4 mL of 2M HCl and transfer to centrifuge tube with DI water

___ Proceed to Appendix 4 for Am/Cm precipitation

APPENDIX 4

AMERICIUM / CURIUM PRECIPITATION

____ 0.1mL 500mg/L Neodymium and swirl

____ 2mL 49% HF and swirl

____ Wait 30 minutes

____ Filter

PLUTONIUM PRECIPITATION

____ 0.1mL 500mg/L Neodymium and swirl

____ 3 – 4 drops 25% Hydrazine Dihydrochloride and swirl

____ Wait 10 minutes

____ 2mL 49% HF and swirl

____ Wait 30 minutes

____ Filter

URANIUM PRECIPITATION

____ 0.1mL 500mg/L Neodymium and swirl

____ 1.0mL Titanium chloride and swirl

____ Wait 30 seconds

____ 2mL 49% HF and swirl

____ Wait 30 minutes

____ Filter

STANDARD OPERATING PROCEDURE

FOR

PARTICLE SIZE ANALYSIS OF SOILS

(GL-GC-E-119)

PROPRIETARY INFORMATION

Process Owner	(sign and date)	(print name)
Quality Review	(sign and date)	(print name)
Approval and Authorization	(sign and date)	(print name)

DRAFT

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1.0 STANDARD OPERATING PROCEDURE FOR PARTICLE SIZE ANALYSIS OF SOILS

2.0 PURPOSE

This Standards Operating Procedure (SOP) describes the procedures used to quantitatively determine the distribution of particle sizes in soils.

3.0 DISCUSSION

The distribution of particle sizes larger than 75 um (retained in the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 um is determined by a sedimentation process, using a hydrometer to secure the necessary data.

4.0 DEFINITIONS

4.1 All terms used in this SOP are familiar to the general lab population.

5.0 PROCEDURE

5.1 Refer to ASTMD 422-63 (Reapproved 2002) "Standard Test Method for Particle Size Analysis of Soils".

6.0 CALCULATIONS

6.1 Refer to ASTMD 422-63 (Reapproved 2002) "Standard Test Method for Particle Size Analysis of Soils". (Calculations - sections 12-16)

7.0 DATA VALIDATION AND REVIEW AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for Data Packaging and Validation and GL-LB-E-005 for Data Review/Validation.

8.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

For Safety and Heath Issues associated with this procedure, refer to the Safety, Health and Chemical Hygiene plan GL-LB-N-001.

9.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks are maintained as quality records in accordance with GL-QS-E-008 for the Managements and Disposition of Quality Records.

10.0 LABORATORY WATER HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

11.0 REFERENCES

11.1 ASTMD 422-63 (Reapproved 2002) "Standard Test Method for Particle Size Analysis of Soils".

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

DENSITY

(GL-GC-E-064 REVISION 3)

APPLICABLE TO METHODS:
ASTM D5057

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR DENSITY

2.0 METHOD CODE

ASTM D5057

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure (SOP) describes the method used to determine the density of granules, powders, and water reactive liquids, solids in sludges.

4.0 METHOD SUMMARY

Density is mass per unit volume. Density can be calculated by dividing the mass of a specific volume of sample by that volume.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

5.4 Soil

5.5 Sludge

5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is not specified by the method.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples are collected in plastic or glass containers.

7.2 No sample preservatives are required.

7.3 Samples are stored at 4 ± 2° C until analysis. Refer to GL-SR-E-001 for Sample Receipt, Login and Storage.

8.0 INTERFERENCES/LIMITATIONS

8.1 The analyst should determine whether the sample falls under Group A, B, or C.

8.1.1 Group A materials: free-flowing liquids

8.1.2 Group B materials: Granules, powders, and water reactive liquids, solids, or sludges.

8.1.3 Group C materials: Bulk solids (such as gravel, paper, or wood)

8.2 If the sample falls under Group A or Group C, refer to SOP GL-GC-E-065 for the Specific Gravity method.

8.3 Density can only be analyzed on Group B materials.

9.0 PERFORMANCE CHARACTERISTICS

Method precision: Limited to the precision of the balance and graduated cylinder used to measure sample mass and volume.

10.0 DEFINITIONS

10.1 Mass - A physical property that represents the quantity of matter in a body.

10.2 Weight - The force a body exerts because of the pull of gravity on the mass of that body.

NOTE: In this SOP mass and weight are used as synonymous terms.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze samples without supervision until trained by qualified personnel and upon the successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data is obtained, it is recorded in the AlphaLIMS

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear safety glasses while in the laboratory.

13.2 All chemicals and samples should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents are maintained in the laboratory. Individual sample MSDS forms provided by the clients are kept in login.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The list is typically in the form of a computer-generated batch sheet and is placed on the clipboard outside of the main cooler. The sample custodian removes the appropriate samples from the cooler and scans them to ALPHALIMS using a bar code scanner. The analyst then takes custody of the samples and scans the batch to the code for the area where the samples are to be prepped or analyzed.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Analytical Balance capable of weighing to 0.01 g.

NOTE: Balances are calibrated in accordance with GL-LB-E-002 for Balances.

15.2 Graduated cylinders - Cylinder size depends on matrix and amount of sample. Recommended sizes: 10, 25, 50, and 100 mL.

16.0 REAGENTS

ASTM type II deionized (DI) water

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

Not Applicable

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Not Applicable

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

A matrix duplicate is run for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples.

20.2 Acceptance limits: Refer to current SPC control limits

21.0 SUGGESTED RUN SEQUENCE

21.1 Sample

21.2 Sample duplicate

21.3 Sample 2 - x where x $\leq$ 10

21.4 Repeat steps 21.1 through 21.3 for every group of 10 samples.

22.0 PROCEDURE

22.1 Place a graduated cylinder on an analytical balance.

NOTE: Never touch the graduated cylinder with your bare hands. Always use a Kimwipe or tongs

22.1.1 Enter container weight on Density data entry screen.

22.2 Fill the graduated cylinder to the maximum volume with DI H_20.

22.2.1 Enter this weight on the density data entry screen.

22.2 Fill the graduated cylinder to the maximum volume with DI H_20.

22.2.1 Enter this weight on the data entry screen.

22.2.2 Discard water and dry the graduated cylinder.

22.3 Place the graduated cylinder back on the balance.

22.3.1 Place a aliquot of sample into the graduated cylinder up to the maximum volume mark

22.3.2 Enter this weight on the density data entry screen.

22.3.3 To obtain the aliquot weight, subtract the empty container weight from the sample and container weight. Record this value on the density data entry screen.

22.4 Calculations / Reporting of results:

22.4.1 Bulk Density (g/ml)= $(Y)\dfrac{(S - W)}{(R - W)}$

Where:

Y = 1g 1ml, the conversion of mass/vol. at 4°C.

S = Weight of sample-filled container.

R = Weight of water-filled container.

W = Weight of empty container.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, data is made available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Not Applicable

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

Not Applicable

30.0 REFERENCES

30.1 ASTM D 5057-90: Standard Test Method for Screening Apparent Specific Gravity and Bulk Density of Waste. Vol 11.04.

30.2 Standard Methods for the Examination of Waste and Wastewater, 18th ed. p 2-86, Part 2710 f. (1992).

30.3 Moeller, Therald et al., Chemistry with Inorganic Qualitative Analysis Second Edition, Academic Press Inc., 1984, page 21.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

SAMPLE RECEIPT, LOGIN AND STORAGE

(GL-SR-E-001 REVISION 17)

GEL's Document Control Officer certifies this document to be a true copy of the fully executed original.

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1.0 STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIPT, LOGIN AND STORAGE

2.0 PURPOSE

To describe the routine operational procedures for the receipt, login and storage of samples received by General Engineering Laboratories, LLC (GEL).

3.0 DISCUSSION

3.1 Sample custody is a pre-planned mechanism for tracking a sample from the collection of the sample in the field through the release of the finished analytical data to the client. At the collection site, the sample containers are filled with sample and the Chain of Custody form is initiated. The sample collector fills out the form, which includes the name of the client, the requested analysis parameters, sample location, the date and time of collection, sampling technique, preservatives used, and any comments or remarks that may be useful in the analytical work or data interpretation that will follow. Proper sample receipt, login and storage assure accurate chain of custody.

3.2 Custody is defined as:

3.2.1 Being in your physical possession, or
3.2.2 Being in your view, after being in your possession, or
3.2.3 Being locked up after being in your possession, or
3.2.4 Being in a designated secure area

3.3 Upon arrival at the laboratory, sampling personnel, delivery service and carriers relinquish the samples to the sample management group. Each sample container receives a unique sample identifier that is assigned electronically by LIMS (Laboratory Information Management System). LIMS tracks the status and location of each sample container, and serves as the database for analytical results.

4.0 DEFINITIONS

4.1 ALPHALIMS: Laboratory Information Management System.

4.2 Chain of Custody (COC): A written record of sample transfer and possession.

4.3 Custody Seal: Security seals that are attached to sample containers and/or bottles that are used to detect unauthorized tampering.

4.4 Holding Time: The period of time between sample collection and preparation or analysis.

4.5 Labeled Package: A package containing radioactive material labeled with a Radioactive White-I, Radioactive Yellow-II or Radioactive Yellow-III label as specified in US Department of Transportation Regulations, 49 CFR 172.403 and 172.436-440.

4.6 Matrix: The physical appearance or make-up of a sample (groundwater, drinking water, wastewater, soil, sludge, etc.) as determined by the client or Project Manager.

4.7 Material Safety Data Sheet (MSDS): A document that may accompany samples of known chemical characteristics. (See our “Safety, Health and Chemical Hygiene Plan” for more information on MSDSs.)

4.8 Preservative: Additives that are introduced to a sample at the time of collection to help retard chemical and biological changes that may occur.

4.9 Turn Around Time (TAT): A numeric designation to the degree of attention a sample should receive. This designation is used to convey the client's requested data delivery dates to the laboratory.

4.10 Sample Delivery Group (SDG): One or more samples (typically not to exceed 20 samples) from a specific client that are reported by the laboratory at the same time.

4.11 Sample Receipt Review (SRR): A form used to document a sample's arrival and the condition of its arrival at the laboratory.

4.12 Sample: Any item that has been submitted for analysis to GEL.

5.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

5.1 All samples must be handled with care during the login process. Wear protective gear such as gloves, aprons, safety glasses and laboratory coats when handling all samples. Some samples may be accompanied by MSDSs that contain vital information on potential hazards. The sample description and client labels may also give this information.

NOTE: Gloves and protective eyewear must be worn when handling samples. Lab coats should be worn when handling any samples but are only required to be worn when handling radioactive or hazardous samples. (Refer to the "Safety, Health and Chemical Hygiene Plan.")

5.2 If there is a spill of a known hazard (based on historical results, MSDSs, and/or sample description), immediately contact the Group Leader, Laboratory Waste Manager, or Radiation Safety Officer as appropriate.

5.3 All sample management personnel are required to read and understand GEL's "Safety, Health and Chemical Hygiene Plan," which is found on GEL's Intranet.

6.0 PROCEDURES

6.1 Sample Package Receipt

6.1.1 All sample packages submitted to GEL are received by sample management personnel. Samples are received from a number of carriers including GEL field staff, GEL couriers, individual clients, and public and private shipping companies.

6.1.2 Upon arrival, all sample packages will be inspected for integrity. Note any unusual physical damage, signs of leakage, or evidence that custody seals have been tampered with. If the package appears to be leaking or has any unusual odor, place it under the fume hood and notify the Group Leader, Laboratory Waste Manager, Radiation Safety Officer, or Project Manager as appropriate before continuing.

6.1.3 All sample packages will also be screened for external contact radiation exposure. This screening is performed to determine the possible presence of radionuclides that may require special handling. If a radioactive "labeled" package is received, or any package exceeds 0.5 mrem/hr on contact, the RSO group should be notified, and the package is segregated in the GEL sample receiving area where the RSO or designee will unpack the package following the procedures described in GL-RAD-S-007 for "Receiving of Radioactive Samples."

6.1.4 Bioassay and Low Level Mercury (LLHG) sample packages are initially received and segregated in the GEL login area. Following package screening, they are then transported to the bioassay or LLHG login area for inspection, login and storage. Bioassay and LLHG receiving staff perform the same sample inspection, login and storage procedures using the Sample Receipt Review (SRR) in Appendix 2 or 3 as applicable, except as noted in Section 6.1.7.

6.1.5 Packages indicating <0.5 mrem/hr should be further segregated to identify samples intended to be received under the authority of GEL's Radioactive Material License. In addition to "Labeled" radioactive material, radioactive material is any material that meets the following criteria:

6.1.5.1 Any Material received that was shipped as DOT Hazard Class 7 Limited Quantity- Excepted Package.

6.1.5.2 Any material shipped and received that is marked as radioactive (i.e. conventional trefoil, yellow and magenta tape, etc.), or has otherwise been declared radioactive by the consignor in the accompanying documents. This material may be intended for receipt under the authority of a radioactive materials license although it was shipped under DOT exemption for radioactive material.

6.1.6 All discrepancies noted during receipt and inspection shall be recorded using a Sample Receipt Review (SRR) form in Appendix 2.

6.1.6.1 As required client specific Sample Receipt Review forms may be created by the Project Management Group. These checklists are created because additional sample management comments and checks are required in order to meet quality objectives established for these project samples.

6.1.7 Open all shipping containers (excluding bioassay & LLHG samples) under the high volume exhaust duct located in Sample Receiving. (NOTE: It is only necessary to open Bioassay & LHG samples under a fume hood when the integrity of the containers is suspected/determined to be compromised.)

6.1.7.1 All samples received (excluding bioassay) must be screened for radioactivity using a Geiger-Muller pancake probe. Results for the highest reading samples are to be noted on the SRR form. The Radiation Safety Group shall be notified when readings for any individual non-radioactive sample exceed 2x area background.

6.1.8 The COC should accompany all samples received by the Sample Management Group. The COC documentation includes sample identification (e.g., MW-1; Lagoon 17; #1234567), sampling date and time, sample collector, and requested parameters to be tested. If this documentation is not present, the Sample Management Group upon receipt shall initiate the COC. Identify this initiation by printing "INITIATED ON RECEIPT" on the COC form.

6.1.9 Compare the sample labels to the Chain of Custody; compare sample descriptions, collection dates, collection times, number of containers and any other available information. Note any discrepancies of the COC and the Sample Receipt Review form (SRR), and inform the Project Manager. Sign and date (including time) the COC in the appropriate box.

6.1.10 Analytical procedure may require preservation of the sample to ensure that changes in the samples chemistry or biology do not occur. The two predominant preservation techniques used are changing the pH of the sample and cooling the sample to about 4°C. It is important to check and document the holding time, preservation and temperature of the samples upon arrival to the laboratory. The correct methods of sample storage, chemical preservation, and maximum holding times are shown in Appendix 1. Those samples determined to be non-conforming shall be documented and the Project Manager notified.

Verify and document pH preservation using the following procedure:

6.1.10.1 Open the container.

6.1.10.2 Pour an aliquot of the original sample into a secondary container. Immerse a pH strip into the secondary container to take the measurement.

6.1.10.3 Observe the pH as indicated on the pH strip, and discard pH strip and secondary container.

NOTE: Never reuse a pH strip or one that has been contaminated.

6.1.10.4 Document results of the preservation verification on the appropriate line of the Sample Receipt Review form. (See Appendix 2 for example of a Sample Receipt Review form.)

NOTE: If the pH of the sample is determined to be non-conforming, place the sample on hold and notify the Project Manager. The Project Manager will call the client for further direction. If direction is given to adjust the preservation, continue processing the sample, and preserve the sample with the appropriate preservative (Appendix 1) recording the lot # of preservative used on the SRR. After adding the appropriate preservative to the sample, wait 2 minutes and perform steps 6.1.10.1 - 6.1.10.4 again. The preserved sample should now be placed on the preservation adjustment hold shelf located in the main cooler. This ensures that the 16-hour holding time for metals samples and the 24-hour holding time for radiochemistry samples is met following preservation or adjustment. Document this on the SRR: "SAMPLE PRESERVED UPON ARRIVAL."

6.1.10.6 Following is a list of tests that require pH verification upon arrival:

TEST	**pH**
Ammonia	<2
COD	<2
Cyanide	>12

Hardness	<2
Hydrazine	<2
Metals	<2
Nitrate/Nitrite	<2
Phenols	<2
Phosphates, Total	<2
Radiochemistry (all except Tritium, C-14, Rn-222, I-129, I-131)	<2
Sulfide	>9
TKN	<2
TOC/TIC/DOC	<2

NOTE: The pH of all aqueous sample fractions, preserved and unpreserved, shall be checked during sample login for the following DOE Albuquerque (DOE-AL) installations: (Exceptions to the pH check are Rn-222, tritium, iodine, VOC, TOX, oil and grease, and urine samples.)

- Los Alamos National Laboratories
- Mound Plant
- Pantex Plant
- Sandia National Laboratories, Albuquerque
- Sandia National Laboratories, Livermore

6.1.10.7 Sample receipt temperature is verified and documented upon using the following procedure:

6.1.10.7.1 Open the sample cooler.

6.1.10.7.2 Remove the Temperature Validation Container (TVC) if provided.

6.1.10.7.3 Open the TVC and immerse a thermometer with a valid calibration into the TVC.

6.1.10.7.4 Allow the thermometer reading to equilibrate, and read the thermometer result while it is still immersed in the TVC.

6.1.10.7.5 Alternately the receipt temperature can be measured with an infrared temperature (IR) gun with a valid calibration by selecting the TVC or another sample within the shipment.

6.1.10.7.6 Record the observed reading on the Sample Receipt Review form (Appendix 2), as well as on the COC if a space is provided: i.e. “TEMP. 4° UPON ARRIVAL.”

6.1.10.7.7 Temperature verification results of 4° ± 2°C, are considered conforming for those samples listed in Appendix 1 for 4°.

6.1.10.7.8 If the initial temperature verification results are determined to be non-conforming, select another sample container from the shipment for temperature verification and re-perform steps.

6.1.10.7.9 Record the verification temperature on the SRR as well as on the COC if a space is provided. Label the temperature as a verification temperature (i.e., VT=7°C).

6.1.10.7.10 If another container is not available within the shipment to verify the temperature, the secondary temperature verification is not performed and duly noted.

6.1.10.8 Project Managers may specify via client specific SRRs that aqueous organic analysis sample containers (excluding volatile 40-mL vials) be checked for the presence of chlorine residual at the time of sample receipt. If chlorine residual is present, document as such on the SRR and inform the Project Manager. The Project Manager may specify that samples with chlorine residual require the addition of $Na_2S_2O_3$.

6.1.11 Deliver the completed COC and SRR to the appropriate Project manager.

6.1.12 The Project Manager or Project Manager Assistant “logs” the data from the COC and SRR into ALPHALIMS. Once samples are logged into the system, unique bar code labels are generated for each sample container.

6.1.13 The bar code labels are ready to be affixed to the appropriate containers.

6.1.14 Sample bar code labels are color-coded as follows:

6.1.14.1 Yellow and magenta for radioactive samples.

6.1.14.2 Solid white for Federal Division non-radioactive samples

6.1.14.3 White and green for Industrial Division samples.

6.1.15 Compare the sample description on the printed GEL bar code label to the client sample bottle label before attaching labels to containers. You should not cover the client’s label or any other information provided by the client or sample collector.

6.1.16 If the sample is a solid submitted for volatiles analysis and a single container is provided, a designation is generated on the barcode label indicating, “Volatiles must aliquot sample first.” It is then stored in the appropriate volatile cooler until removed for volatiles testing. Once the volatiles lab takes its required aliquot the container will be marked with the analyst’s initials and the date completed. The sample container will then be placed in the appropriate walk in cooler and released for other laboratory analyses. Note exception in Section 6.2.2.1.

6.2 Sample Storage and Security

6.2.1 Once the samples have been properly labeled, the samples are placed in the appropriate storage areas. The storage areas are located within the laboratory area of the building. Access to the laboratory is limited to those with security clearance identification badges. Entrance into the laboratory is electronically monitored. All visitors to the building must sign in at the reception area where they will receive "Visitor" identification badges. Visitors must be escorted while they are in the laboratory.

The samples are scanned into the electronic tracking system. Containers are loaded into the system by container type and size (i.e., 1000 mL – nalgene), preservative (i.e., H_2S0_4), and storage area of destination.

6.2.2 Samples are placed in numerical order in the appropriate storage locations throughout the facility.

6.2.2.1 Samples requiring analysis of volatile organics shall be segregated from other samples by placing them in either the radioactive or non-radioactive coolers, which are located in the Volatiles area and maintained at 4° ± 2°C.

NOTE: Samples requiring volatile analyses known to contain high concentrations of organic solvents or hydrocarbons should not be stored in the volatiles coolers. Place these samples in either the general use walk-in cooler.

6.2.2.2 Samples requiring radiochemical analyses only (except radon) are stored, in numerical order, in ambient storage. Radioactive and Non Radioactive sample are segregated in these storage areas.

6.2.2.3 Samples required cold preservation (other than volatile organics samples) are stored, in numerical order, in general use walk-in coolers, which are maintained at 4° ± 2°C. Radioactive and non-radioactive samples are segregated in these storage areas.

6.2.3 The Sample Management Group monitors cooler temperature twice daily, every working day. Calibrated thermometers are located in each walk-in cooler and readings are taken once in the morning and once in the afternoon, no less than two hours apart. Contact the Group Leader if temperatures fall outside of acceptance ranges. Document all non-conformances and corrective actions in the temperature logs.

7.0 RECORDS MANAGEMENT

7.1 The Sample Receipt Review form is attached to the Chain of Custody and forwarded to the Project Manager.

7.2 Cooler temperature logs are reviewed each month by Quality Systems. At the end of the year, completed logs are forwarded to Quality Systems for archiving.

8.0 REFERENCES

8.1 Example Standard Operating Procedures for Contract Laboratory Program (CLP), National Enforcement Investigations Center (NEIC), Contract Evidence Audit Team (CEAT-TechLaw), EPA Contract 68-01-6838, 1986.

APPENDIX 1: STORAGE AND PRESERVATION

SAMPLE STORAGE AND PRESERVATION REQUIREMENTS

Parameter	Container[1]	Preservation	Holding Time[2]
Inorganics			
Acidity	P,G	$4^{Of}C$	14 days
Alkalinity	P,G	$4^{O}C$	14 days
Demand (BOD)	P,G	$4^{O}C$	48 hours
Bromide	P,G	None	28 days
Chemical Oxygen Demand (COD)	P,G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Chlorine by Bomb	P,G	None	None
Chloride	P,G	None	28 days
Color	P,G	$4^{O}C$	48 hours
Conductivity	P,G	$4^{O}C$	28 days
Corrosivity by pH	**P**	**None**	**Immediate**
Corrosivity to Steel	P	None	None
Cyanide amenable to chlorination	P,G	$4^{O}C$, NaOH to pH>12, 0.6g ascorbic acid [3]	14 days [4]
Cyanide, total	P,G	$4^{O}C$, NaOH to ph>12, 0.6g ascorbic acid [3]	14 days [4]
Dissolved Oxygen	**G (bottle and tap)**	**None**	**Immediate**
Fixed and Volatile Solids	P,G	$4^{O}C$	7 days
Flashpoint	P,G	None	None
Fluoride	P	None	28 days
Hardness	P,G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
Heating Value	P	None	None
Hydrazine	**G**	**HC1 to pH<2**	**Immediate**
Percent (%) Moisture	P	$4^{O}C$	None
Ammonia Nitrogen	P,G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Nitrate	P,G	$4^{O}C$	48 hours
Nitrite	P,G	$4^{O}C$	48 hours
Nitrate/Nitrite	P,G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Total Kjeldahl and Organic Nitrogen	P,G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Odor	**G**	**$4^{O}C$, Zero headspace**	**Immediate**
Oil and Grease	G	$4^{O}C$, HC1 or H_2SO_4 to pH<2	28 days
Orthophosphate	**P,G**	**Filter immediately, $4^{O}C$**	**48 hours**
Total Phenols	G	$4^{O}C$, H_2SO_4 to pH<2	28 days
pH	**P,G**	**None**	**Immediate**
Total Phosphorus	P,G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Residual Chlorine	**P,G**	**None**	**Immediate**
Salinity	P	None	28 days
Specific Gravity	P	$4^{O}C$	7 days
Sulfate	P,G	$4^{O}C$	28 days
Sulfide	P,G	$4^{O}C$, add ZNAce and NaOH to pH>9	7 days
Sulfite	**P,G**	**None**	**Immediate**
Sulfur by Bomb	G	None	None
Surfactants	P,G	$4^{O}C$	48 hours
Settleable Solid	P,G	$4^{O}C$	48 hours
Total Dissolved Solid	P,G	$4^{O}C$	7 days
Total Solid	P,G	$4^{O}C$	7 days
Total Suspended Solid	P,G	$4^{O}C$	7 days
Volatile Solid	P,G	$4^{O}C$	7 days
Total Organic Carbon	P,G	$4^{O}C$,HCl or H_2SO_4 to pH<2	28 days
Total Organic Halides	G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Total Petroleum Hydrocarbons	G	$4^{O}C$, H_2SO_4 to pH<2	28 days
Turbidity	P,G	$4^{O}C$	48 hours
Metals (except chromium VI and mercury)	P	$4^{O}C$,HNO_3 to pH<2	6 months
Chromium VI - Aqueous	P	$4^{O}C$	24 hours

Chromium VI - Solids	P	$4^{O}C$	7 days for extraction
Mercury - Wastewater and Drinking water	P,G	$4^{O}C$,HNO_3 to pH<2	28 days
Mercury - Others	G	$4^{O}C$,HNO_3 to pH<2	28 days
<u>Bacteriology</u>			
Coliform, fecal	P,G	4, 0.008% $Na_2S_2O_3$ [3]	6 hours
Standard Plate Count	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	24 hours
Coliform, total - Wastewater	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	6 hours
Coliform, total - Groundwater	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	24 hours
<u>Organics</u>			
Base/Neutral and Acid Extractables - Water	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
Base/Neutral and Acid Extractables - Solid and Waste	G, teflon-lined cap	$4^{O}C$	14 days for extraction 40 days after extraction for analysis
Base/Neutral and Acid Extractables - Concentrated Waste	G, teflon-lined cap	None	7 days for extraction 40 days after extraction for analysis
BTEX - Solid and sludge	G, teflon-lined septum	$4^{O}C$	14 days
BTEX - Water	G, teflon-lined septum	$4^{O}C$, 0.008% $Na_2S_2O_3$, zero headspace	14 days
TPH-GRO	G, teflon-lined cap	$4^{O}C$, HCl to pH s, zero headspace	14 days
TPH-DRO	G, teflon-lined cap	$4^{O}C$	14 days
Volatiles - Groundwater	G, teflon-lined cap	$4^{O}C$, HCl to pH s, zero headspace	14 days
Chlorinated Herbicides - Water	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
Chlorinated Herbicides - Solid and Waste	G, teflon-lined cap	$4^{O}C$	14 days for extraction 40 days after extraction
Volatiles - Drinking Water	G, teflon-lined cap	$4^{O}C$, 0.008% $Na_2S_2O_3$[3], zero headspace	14 days
Volatiles (excluding 2 chloroethylvinylether) - Wastewater	Encore Sampler	$4^{O}C$, zero head-space, HC1 to pH 2	14 days
Volatiles - Wastewater	G, teflon-lined cap	$4^{O}C$, 0.008% $Na_2S_2O_3$[3], zero headspace	7 days
Volatiles - Solid and Sludge -	Encore Sampler	$4^{O}C$	14 days
Volatiles - Concentrated Waste	G, teflon-lined septum	None	14 days
Industrial Solvents	G, teflon-lined septum	$4^{O}C$	None
Organochlorine Pesticides and PCBs	Amber G, teflon-lined cap	$4^{O}C$ 0.008% sodium thiosulfate solution	7 days for extraction 40 days after extraction for analysis
PCBs in Oil	G, teflon-lined cap	None	7 days for extraction 40 days after extraction for analysis
Dioxin	G, teflon-lined cap	$4^{O}C$	7 days for extraction 40 days after extraction for analysis
Total Petroleum Hydrocarbon	G, teflon-lined septum	$4^{O}C$	14 days
Coliform, total - Drinking water	P,G	$4^{O}C$, 0.008% $Na_2S_2O_3$	30 hours
<u>Radiochemistry</u>			
Carbon-14 - Water and Soil	P	$4^{O}C$	6 months
Gamma Isotopes - Water	P	HNO_3 to pH-2	6 months
Gamma Isotopes - Soil	P	None	6 months
Gross Alpha and Beta - Water	P	HNO_3 to pH-2	6 months

Gross Alpha and Beta - Soil	P	None	6 months
Iodine-129 - Water and Soil	P	None	6 months
Iodine -131 - Water	P	None	6 months
Neptunium - Water	P	HNO_3 to pH-2	6 months
Neptunium - Soil, Vegetation, and Air Filters	P	None	6 months
Plutonium - Water	P	HNO_3 to pH-2	6 months
Plutonium - Soil, Vegetation, and Air Filters	P	None	6 months
Thorium - Water	P	HNO_3 to pH-2	6 months
Thorium - Soil, Vegetation, and Air Filters	P	None	6 months
Uranium - Water	P	HNO_3 to pH-2	6 months
Uranium - Soil, Vegetation, and Air Filters	P	None	6 months
Americium - Water	P	HNO_3 to pH-2	6 months
Americium - Soil, Vegetation, and Air Filters	P	None	6 months
Curium - Water	P	HNO_3 to pH-2	6 months
Curium - Soil, Vegetation, and Air Filters	P	None	6 months
Lead-210 - Water	P	HNO_3 to pH-2	6 months
Nickel-59 - Water and Soil	P	None	6 months
Nickel-63 - Water and Soil	P	None	6 months
Phosphorus-32 -Water	P	HNO_3 to pH-2	6 months
Phosphorus-32 -Soil	P	None	6 months
Polonium -Water	P	HNO_3 to pH-2	6 months
Polonium -Soil	P	None	6 months
Promethium-147 -Water	P	HNO_3 to pH-2	6 months
Promethium-147 -Soil	P	None	6 months
Radium-223 - Water	P	None	6 months
Radium-224 - Water	P	None	6 months
Radium-226 - Water	P	HNO_3 to pH-2	6 months
Radium-228 - Water	P	HNO_3 to pH-2	6 months
Radon-222 - Water	40ml volatile bottle	$4^{O}C$, Zero headspace	7 days
Radon-222 - Soil	P	$4^{O}C$	6 months
Strontium-89/90 -Water	P	HNO_3 to pH-2	6 months
Strontium-89/90 -Soil	P	None	6 months
Technetium-99 -Water	P	HNO_3 to pH-2	6 months
Technetium-99 -Soil	P	None	6 months
Total Alpha Radium -Water	P	HNO_3 to pH-2	6 months
Total Alpha Radium -Soil	P	None	6 months
Total Uranium -Water	P	HNO_3 to pH-2	6 months
Tritium - Water, Soil, Vegetation, and Air Filters	P	$4^{O}C$	6 months
Iron 55 -Water	P	HNO_3 to pH-2	6 months
Iron 55 -Soil	P	None	6 months
Total Uranium -Soil	P	None	6 months

[1] P = Polyethylene; G = Glass
[2] Samples should be analyzed as soon as possible after collection. The holding times listed are maximum times that samples may be held before analysis and be considered valid.
[3] Used only in the presence of residual chlorine.
[4] Maximum holding time is 24 hours when sulfide is present. All samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If present, remove by adding cadmium nitrate powder until a negative spot test is obtained. Filter sample and add NaOH to pH12.

APPENDIX 2: SAMPLE RECEIPT REVIEW SHEET

GENERAL ENGINEERING LABORATORIES, LLC

SAMPLE RECEIPT & REVIEW FORM

PM use only

Client:	SDG/ARCOC/Work Order:
Date Received:	PM(A) Review (ensure non-conforming items are resolved prior to signing):
Received By:	

	Sample Receipt Criteria	Conforming	NA	Non-Conforming	Comments/Qualifiers (Required for Non-Conforming Items)
1	Shipping containers received intact and sealed?				Circle Applicable: seals broken damaged container leaking container other (describe)
2	Samples requiring cold preservation within (4 +/- 2 C)? Record preservation method.				Circle Temp device serial # ice bags blue ice dry ice none other(describe)
3	Chain of custody documents included with shipment?				
4	Sample containers intact and sealed?				Circle Applicable: seals broken damaged container leaking container other (describe)
5	Samples requiring chemical preservation at proper pH?				Sample ID's, containers affected and observed pH:
6	VOA vials free of headspace (defined as < 6mm bubble)?				Sample ID's and containers affected:
7	Samples received within holding time?				Id's and tests affected:
8	Sample ID's on COC match ID's on bottles?				Sample ID's and containers affected:
9	Date & time on COC match date & time on bottles?				Sample ID's affected:
10	Number of containers received match number indicated on COC?				Sample ID's affected:
11	COC form is properly signed in relinquished/received sections?				
12	Air Bill ,Tracking #'s, & Additional Comments				

Radiological Information	Non-RAD	RAD	RADI	RSO RAD Receipt #
What is the radiological classification of the samples?				Comments:
Radioactivity Screening Results (maximum observed CPM)				*If > x2 area background is observed on a non-radioactive sample, contact the RSO to investigate.

PM (or PMA) review of Receiving Rad classification: ____________________ Initials __________________ Date

APPENDIX 3

BIOASSAY SAMPLE RECEIPT REVIEW

CLIENT____________________

GEL COOLER ______________ CLIENT COOLER_______________ OTHER__________

SAMPLE REVIEW CRITERIA YES NO COMMENTS/QUALIFIERS

Were shipping containers received intact and sealed?			
Were chain of custody documents included?			
Were chain of custody documents completed correctly?			
Were all sample containers properly labeled?			
Were all sample containers received?			
Were samples received within holding time?			
Were the sample containers 500 mL or less?			
For KHCO - Did the sample ID and the customer number match the			
Chain of custody?			

Signature:__________________________________ Date:________________________

ATTACHMENT D-3

GEOCHEMICAL TECHNOLOGIES CORPORATION

STANDARD OPERATING PROCEDURE

Measurement of $^{11}B/^{10}B$ Isotopic Ratio Using Thermal Ionization Mass Spectrometry

Standard Operating Procedures

Laboratory Acceptance

Clients with new projects should not send samples without prior approval from the Boron Isotope Laboratory. Project approval will consist of defining the number of samples, the required precision and timeframe for analysis, description of the project objectives, and signed contract with method of payment defined. Samples will not be accepted without prior approval to ship.

Sample Shipping

Unless prior arrangements are made samples are shipped to GTC at client's expense. Shipping coolers and sample bottles may be provided by the laboratory for an additional charge but are in general readily available and less expensively obtained by client. Client should collect samples in plastic bottles (polyethylene, polycarbonate, etc. is adequate) with screw on caps. Samples should be filtered through a 0.45 micrometer effective pore diameter cellulose acetate filter or equivalent. Preservation with acid should be avoided, and chilling is not required. Caps should be closed tightly and sealed with electrical or similar elastic tape. Bottle labels should clearly indicate sample name, date, client, and note any added preservation. Samples should be placed in a plastic cooler for protection, chain of custody forms or list of samples enclosed, then shipped to the following address:

> Geochemical Technologies Corporation, 4855 Ward Road, Suite 200,
> Wheat Ridge, CO 80033 (Telephone 303 423-8187; E-mail: gtc@att.net).

Sample Handling

Samples will be logged in, Chain of Custody forms signed when necessary, assigned a laboratory tracking number, and examined for condition. Unless special circumstances to expedite analysis are approved prior to analysis, samples are analyzed in order of receipt, with options by the laboratory staff to reorder the sequence in circumstances dictated by the number of samples in a project.

Either clients must provide the analysis for the concentration of boron in each sample or the lab will send the samples out for analysis of boron for a small analytical fee. Samples then begin the separation and extraction procedures required before the final analysis in the mass spectrometer.

Methods

Boron is extracted from solution using a boron specific ion exchange resin, eluted off the column with HCl, purified using an alcohol distillation, and then evaporated to dryness as boric acid. The extracted boron is re-dissolved in sodium carbonate, placed on a tantalum filament, and then the ratio of ^{11}B to ^{10}B is measured in a Thermal Ionization Mass Spectrometer (TIMS).

Results

The mean value of 50 measured ratios is reported as measured, in addition a computed delta ^{11}B relative to the NBS (NIST) Standard Reference Material SRM 951 is also provided for each analysis. Machine bias and accuracy are determined by analyzing the NBS standard in every batch of samples.

A brief letter report is provided describing any analytical details that should be reported along with the results. Interpretive analysis is available under a consulting arrangement if needed; otherwise, the client is assumed to have sufficient knowledge to evaluate the results for the particular application.

ATTACHMENT D-4

UNIVERSITY OF MIAMI TRITIUM LABORATORY

STANDARD OPERATING PROCEDURES

Low-Level Tritium Analysis by Enrichment and Low-Level Proportional Counting

Tritium Laboratory

Environmental Level Measurements of Tritium, Helium and Chlorofluorocarbons (CFC's)

Introduction

Tritium Analysis

Tritium is the radioactive isotope of hydrogen (half-life of 12.32 years, decay rate of 5.626 % per year). Tritium is produced naturally in the upper atmosphere by cosmic radiation. It can replace hydrogen in H_2-gas, forming HT, and in water, forming HTO. The release of excess tritium into the atmosphere from nuclear weapons tests conducted between 1952 and 1963 'tagged' rain water, and thereby all surface waters with HTO. This tracer perfectly follows the water in atmospheric, oceanic and hydrological transport and mixing processes. Atmospheric tritium concentrations peaked between 1962 and 1965 and most of this excess (i.e. bomb produced) tritium was precipitated during the same time period and a few years afterward. Since then the deposition rate has tapered off sharply. Thus the presence of excess tritium in the water of an aquifer unequivocally proves that recharge occurs on a time scale of years to decades. The actual tritium level, combined with approximate local tritium history of precipitation may give more specific information about the make-up of the aquifer.

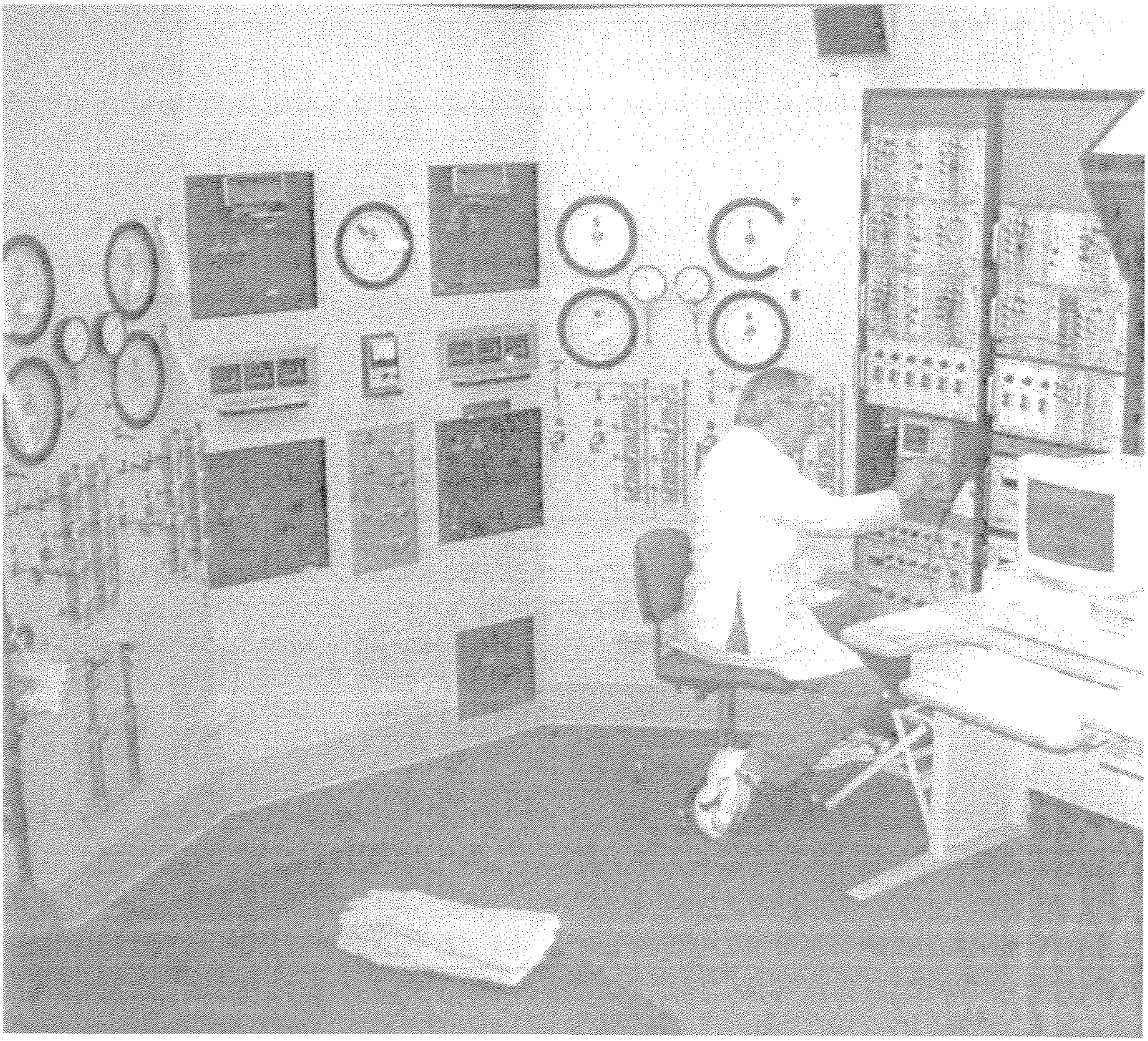
The Tritium Laboratory was originally established in 1960 as a radiocarbon dating facility for ocean waters and sediments. In 1964, it was expanded to perform low-level measurements of environmental tritium, mainly for oceanographic purposes. Due to lessening demand from oceanography, we are now able to offer low-level tritium measurements to other fields such as hydrology. Our present yearly capacity is about 2500 tritium measurements on water samples relating to research projects mainly from the hydrological community.

Tritium assay at the very low levels in nature is often given in tritium units (TU), where one TU represents a tritium/hydrogen ratio of 10^{-18}. In water of 1 TU, the specific activity is equal to 3.2 picocuries per liter (pCi L^{-1}) or 7.1 disintegrations per minute per liter (dpm L^{-1}). We measure these very low activities by internal gas proportional counting of H_2-gas made from the water sample. The counting equipment consists of nine ultra-low background proportional gas counters of various sizes, operating in anticoincidence with a surrounding cosmic-ray detector system. The whole system is encased in a 30-ton iron shield. The electronics mainly consist of commercially available instruments modified for our purpose. The entire operation is computerized and includes many quality control features, from sample data input and machine parameter checks to final statistical tests.

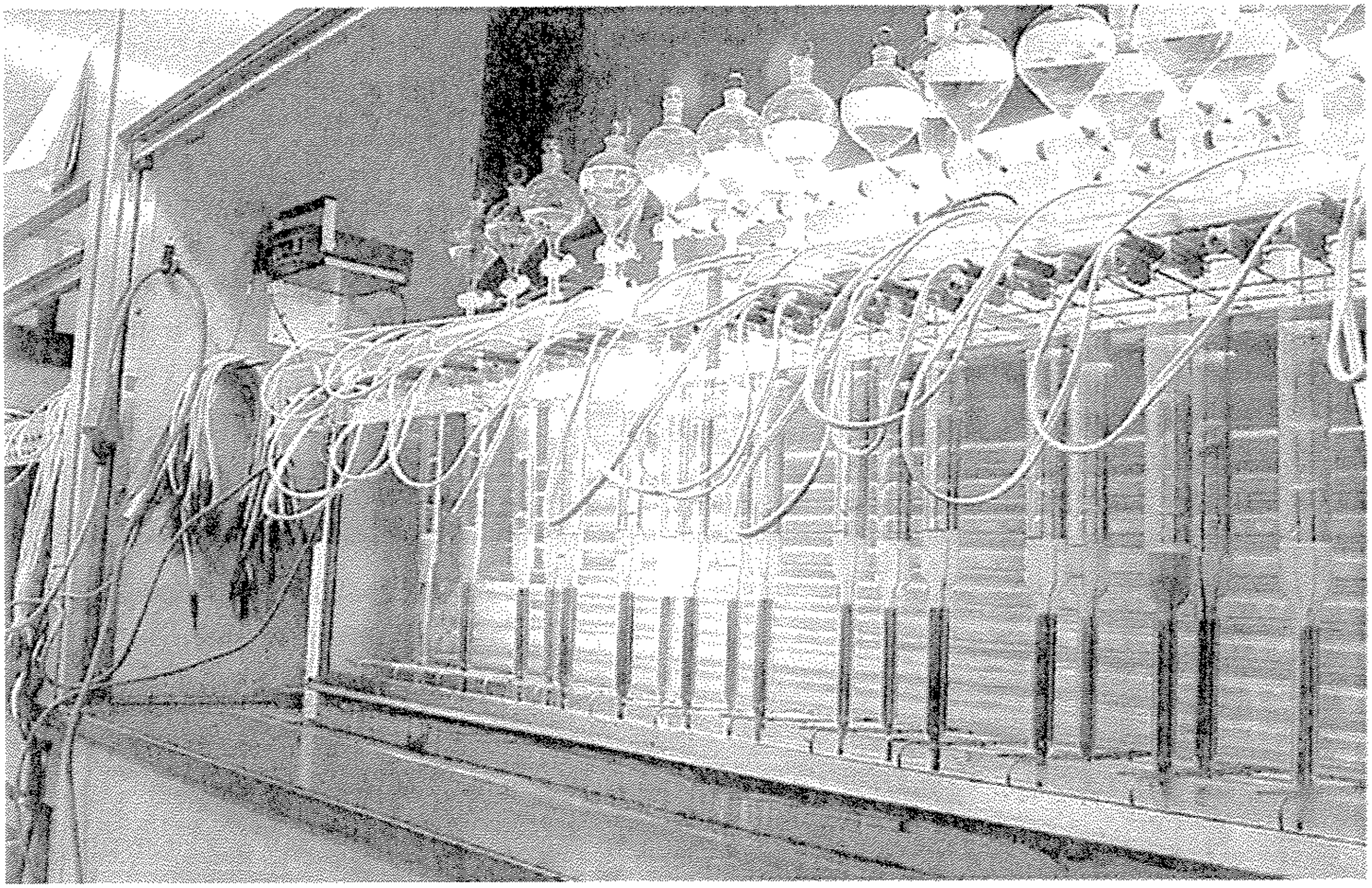
Following conversion to hydrogen gas, "high-level" tritium samples of > 100 TU (300 pCi L^{-1}) may be admitted to counters directly. Low-level hydrological water samples go through an electrolytic enrichment step, in which tritium concentrations are increased about 60-fold through volume reduction. Accuracy of the low-level measurement with enrichment is **0.10 TU (0.3 pCi L^{-1} of H_2O)** , or 3.5 %, whichever is greater; that of low-level counting without enrichment is 3 TU (9.6 pCi $L^{-1}$of H_2O) or 3.5 %, whichever is greater.

Procedures are now available in our Laboratory for measurement of tritium in samples other than ordinary waters.

We routinely do extractions of certain types of H_2O-absorbers used in atmospheric tritium sampling. We also offer the extraction of water from soils and subsequent measurement of tritium in the extracted water. Tritium concentrations in water found in soils, combined with the local precipitation tritium history can be used to estimate the travel time of rainwater through the soil.



The gas proportional counters and electronics are integrated with two microcomputers which maintain rigid quality control testing programs.



Enrichment of tritium in water samples is done by electrolysis. The glass electrolysis cells are housed in a cold water bath during the 10-12 day process.

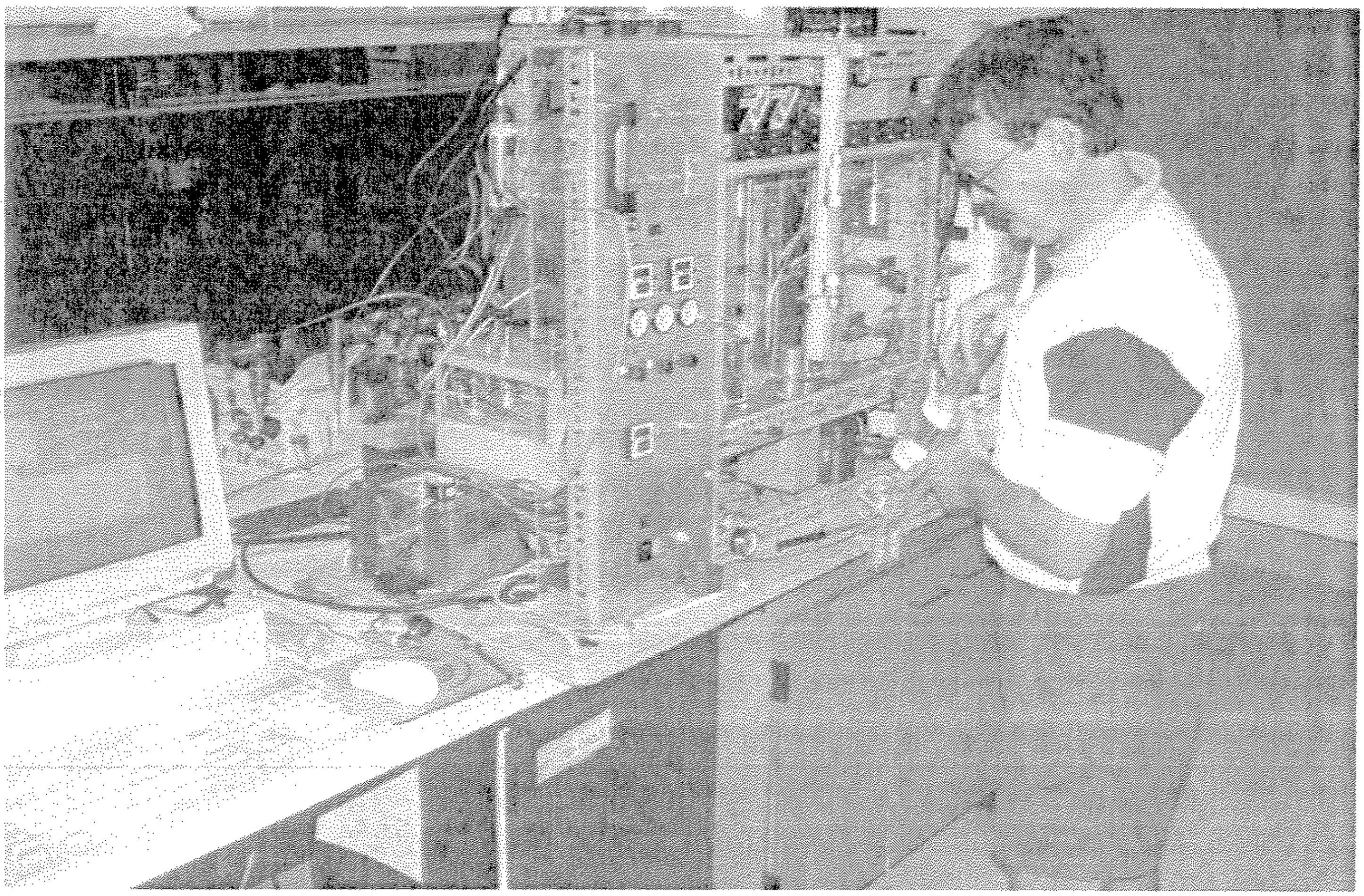
Tritium/Helium-3 Analysis

In cooperation with the University of Miami Noble Gas Laboratory we now also offer the measurement of both tritium and its radioactive decay product, helium-3. The tritium/helium-3 ratio can be used to determine the "age" of a water sample with a resolution of 0.1 years for young (< 40 years old) water. Water "age" is defined as the elapsed time that the water has been isolated from the atmosphere. In a groundwater sample the "age" is equivalent to how long ago the sample was recharged to the aquifer. The Noble Gas Laboratory measures the amount of helium-3 in a water sample using mass spectrometry. Tritium is determined from an additional sample collected at the same time by the helium in-growth method. The water sample for tritium analysis is first degassed to remove any helium-3 and then sealed in a glass container. After the sample is sealed, helium-3 begins to accumulate as tritium decays. After an appropriate time for helium-3 to accumulate (1 week to 1 year depending on the initial tritium concentration) the in-grown helium-3 is measured using mass spectrometry. The tritium concentration in the sample is then determined from the amount of in-grown helium-3, the length of time the sampled was sealed, and the radioactive decay rate (12.4 years) of tritium. Accuracy of the helium in-growth method is 0.01 TU.

Chlorofluorocarbon (CFC) Analysis

The technique of using CFC's as transient tracers to derive estimates of seawater ventilation ages is well established and the use of these tracers to derive estimates of groundwater recharge age is becoming increasingly common. CFCís are potentially useful tracers of groundwater flow because they are non-reactive and their input history is well known. CFC-12 (CCl_2F_2) and CFC-11 (CCl_3F) were introduced into the atmosphere in the late 1940's while CFC-113 (CCl_2FCClF_2) was first released to the atmosphere in the 1960ís. The atmospheric concentrations of these CFCís have been increasing ever since, although CFC-11 and CFC-113 concentrations have leveled off or decreased over the last 5 years (Figure 1) When water is in contact with the atmosphere (i.e. during recharge) it picks up a CFC signature based on the atmospheric concentration and the temperature dependent solubility coefficient of each compound. When isolated from the atmosphere the groundwater retains its characteristic CFC concentration because the compounds are non-reactive (conservative) under aerobic conditions, and relatively little mixing occurs in ground water systems (compared to the ocean). The CFC tracers offer several advantages to the more commonly used tritium/helium-3 tracer pair. CFC-11 and CFC-12 can be used to date groundwater up to 50 years old, while the tritium/helium-3 tracer pair is limited to less than 40 years. CFCís also offer the advantage of essentially real-time data. After receipt of a sample, the typical analysis time is 1 day, while samples for tritium/helium-3 analysis can take from 10 days to several months for complete analysis. Offsetting some of these advantages are the stringent sampling requirements needed to obtain valid CFC-derived recharge ages. For addition information on sampling groundwater for CFC tracer analysis go to: Advice on CFC Sampling .

Water samples are analyzed for CFC's using a custom built purge-and-trap gas chromatograph with electron capture detection. Briefly, water samples are purged with inert gas to remove dissolved gases. The CFCís are adsorbed from the purging gas stream onto trap held at -10^{o} C. Once the CFCís are purged and trapped, the trap is heated to release the CFCís onto a small volume focusing trap held at -15^{o} C. After CFC transfer is complete, the focusing trap is heated releasing the CFC's into the gas chromatograph Separation of the CFC's is achieved on a capillary column and the compounds are detected using a electron capture detector. This method is extremely sensitive and the limit of detection for CFC-11, CFC-12 and CFC-113 is 0.007, 0.01, and 0.01 x10^{-12} moles per kilogram of water (pmol kg^{-1}), respectively. Precision values for all three CFCís are 2 % or less. The accuracy of CFC-derived recharge ages from these measurements is ± 3 years or less.



Injection of a water sample into the custom-built purge-and-trap gas chromatograph for CFC-11, CFC-12 and CFC-113 analysis.

Contact Information

For additional information (Price schedule, procedures, advice on sampling , Tritium Lab staff , *etc.*) please click on the links or contact our laboratory directly:

The Tritium Laboratory
University of Miami/RSMAS
4600 Rickenbacker Cswy.
Miami, Florida 33149-1098, USA

email: Tritium@rsmas.miami.edu
tel: 305/421-4100
fax: 305/421-4112

Last Revised: 6 May 2005

Tritium Laboratory

Price Schedule
Procedures and Standards
Advice on Sampling

TABLE OF CONTENTS

PRICE SCHEDULE

I. SCHEDULE OF COSTS (per sample)

A. Tritium measurement

1. Low-level gas proportional counting of water sample, required sample volume 15 mL. Processing quantity is 4 mL.	**$150.00**

Counting will be performed to ± 3.0 %, one sigma, or ± 3 TU (10 pCi L^{-1}), whichever is larger. Minimum detectable activity (MDA) is 3 TU (10 pCi L^{-1}). For undersized or chemically contaminated samples, special arrangements will have to be made. For samples suspected to be above 1000 TU (3000 pCi L^{-1}), we require advance notice.

2. Enrichment and low-level counting of ultra-low activity water sample, required sample quantity 1000 mL. Normal starting volume is 275 mL.	**$300.00**

Accuracy and precision will be 0.1 TU (0.3 pCi L^{-1}) or ± 3.5 %, whichever is larger. MDA is 0.1 TU (0.3 pCi L^{-1}). For undersized or chemically contaminated samples, special arrangements may have to be made. For samples suspected to be above 30 TU (100 pCi L^{-1}), we require advance notice. NOTE: Stated starting volume is needed for obtaining quoted accuracy: a smaller quantity will usually yield less precise results. For a first run we will take no more than one third of the furnished amount of water unless instructed otherwise by submitter. Combining this analysis with a Helium-3, Helium-4 and Neon analysis (see D1 below) will yield an apparent recharge age of the water.

3. Pre-testing of sample to determine if enrichment is necessary. Required sample volume 1 L.	**$75.00**

Direct counting (as in A.1) will be performed for a set period of time to determine if tritium content is low enough to require prior enrichment. Criterion for enrichment must be provided by submitter beforehand. If sample does not require enrichment, the counting will continue until the criterion under A1 is met and the total cost is the same as above in A.1, i.e. $150.00. If enrichment is required, we have to start from scratch and the cost is sum of A.2. and A.3, i.e. $375.00.

4. Helium in-growth method. Required sample volume 1 L.	**$375.00**

Accuracy and precision will be 0.01 TU. MDA is 0.01 TU. For undersized or chemically contaminated samples, special arrangements will have to be made. A sample is degassed, sealed, and helium-3 allowed to grow in. The in-grown helium-3 is measured by mass spectrometry. The tritium concentration determined from the amount of in-grown helium-3, the length of time the sample is sealed, and the tritium half-life (12.4 years). In-growth time for low level samples can be from 6 to 12 months. Combining this analysis with a Helium-3, Helium-4, and Neon analysis (see D1 below) will yield an apparent recharge age of the water. In most cases method A2 (see above) is recommended. Visit the Noble Gas Laboratory web page for more information regarding this method.

B. Extraction of water absorbers (used in atmospheric tritium sampling)

1. Sieve extraction	**$50.00**
Minimum batch of 4	**$200.00**

Extraction of sieve trap or palladium trap, and restoring of the trap in condition ready for re-use. Trap to be of our standard configuration. Shipping and associated handling not included in price. Cost for tritium analysis of extracted water can be found in section I.A.

2. Extraction of other type traps.	**Price varies**

Extraction of Drierite canister or similar traps. Absorbent is discarded after the process. Price dependent on quantity, configuration and properties of traps. Cost for tritium analysis of extracted water can be found in section I.A .

C. Extraction of water from soils.

1. Extraction of water from soil or rock.	**$100.00**

Water will be removed from sections of soil or rock cores (4 inches maximum diameter, 5.5 inches maximum length) with a vacuum distillation processes. Cost for tritium analysis of extracted water can be found in section I.A.

D. Helium-3 analysis.

1. Helium-3, Helium-4, and Neon analysis.	**$300.00**

^{3}He, ^{4}He and Ne concentrations are determined by mass spectrometry. Special notice is required if the sample is collected from a volcanic area. Water sample must be collected in a custom crimp-sealed copper tube. Copper tubes and clamps are provided upon request. Combining this analysis with a tritium analysis (A2 or A4 above) will yield an apparent recharge age of the water. Visit the Noble Gas Laboratory web page for more information regarding this method.

E. Low Tritium "dead water"

1. Low Tritium "dead water" (< 0.1 TU)	**$30.00 per liter + shipping**

This freshwater is collected from an artesian well that is screened at a depth of ~ 100 m below the water table. Based upon hydraulic conductivity this water has not been in contact with the atmosphere for several thousand years and should therefore contain undetectable amounts of tritium. Analysis of this water by the Tritium Lab indicates that the tritium levels are below our detection limit (< 0.1 TU). The Tritium Lab uses this water for analytical instrument blanks. This water is suitable for use as analytical instrument, field and equipment blanks. The water will be delivered in 1 liter brown glass bottles. Batch analysis available upon request.

F. CFC-11, CFC-12, and CFC-113 analysis.

1. CFC-11, CFC-12, and CFC-113 analysis.	**$150.00**

Water samples are analyzed for CFC's using a custom built purge-and-trap gas chromatograph with electron capture detection. This method is extremely sensitive and the limit of detection for CFC-11, CFC-12 and CFC-113 is 0.007, 0.01, and 0.01 $x10^{-12}$ moles per kilogram of water (pmol kg^{-1}), respectively. Precision values for all three CFC's are 2 % or less. The accuracy of CFC-derived recharge ages from these measurements is ± 3 years or less.

II. SERVICES RENDERED

NOTE: This section and following section do not apply to items I.A.4 and I.D.1. Contact Dr. Zafer Top of the Noble Gas Laboratory (Phone: 305-361-4110, Fax: 305-361-4911, E-mail: ztop@rsmas.miami.edu) for more information regarding these methods.

The University provides the following services:

Discussion on sample quality, sampling techniques, advice to submitters regarding needs and measurement options, and available pertinent reprints, etc. are furnished free.

Upon receiving samples for analysis, the Tritium Lab will:

1. Acknowledge receipt, if client requests.

2. Check inventory of the bottles, syringes or ampules received against a packing list, if supplied. Notify submitter by phone if discrepancy found.

3. Prepare and measure each sample to meet specifications. Unless specifically instructed by the client we will start with no more than one third of the furnished amount of water if a tritium analysis is being perrformed. This will allow for loss of one run and still be enough for duplicate tritium runs, if needed. A CFC analysis requires that the full amount of water in the syringe or ampule be analyzed. The client may want to take two seperate

samples from each source so that there is a backup in case one is lost during analytical processing. The client will not be charged if the CFC sample is lost during analytical processing and a second sample from the same source is not available.

4. Report preliminary results as soon as available, upon phone inquiry by submitter.

5. Issue Data Release with final results. For timing see Description of Procedures and Standards, Section F, Update.

6. Issue an invoice.

7. Save remainder of tritium samples for 3 months. If samples or sample shipping container are to be returned, we will do so using the original container and under one of the following conditions: (1) client sends prepaid shipping labels; or (2) client requests pickup by UPS (known as a "call slip").

8. The Tritium Laboratory will make the best possible effort to deliver correct results. However, since these techniques are on the very fringe of what is technically possible, the University of Miami cannot assume any legal or other responsibility for erroneous results. If submitter can provide a justified reason for suspecting a bad result, we will remeasure such a sample at our cost if the sample quantity remaining with us allows.

III. CONDITIONS

A. Purchase order must be received before work starts. Please inform us when shipping samples so the arrival can be expected.

B. Contract

Due to the increased amount of administrative and legal input needed for a contract, such arrangement may carry a substantial surcharge, the size of which (minimum of 25 %) will depend upon the quantity of administrative and legal work required of the University. Any contract must include, unchanged, the technical and procedural specifications set in this Price Schedule. **The University will not accept any commitments to replace or add to the ones stated in this Price Schedule. The work is a best effort.** Thus, a contract would not change any of the conditions set forth in this Price Schedule.

IV. TECHNICAL CONDITIONS FOR ACCEPTANCE OF TRITIUM SAMPLES

The machinery of the Tritium Laboratory is designed for operation on only extremely low-level tritium water samples and is, therefore, very vulnerable to samples with unexpectedly high tritium activity. It should be remembered that our minimum detection level is below 0.1 TU, i.e. < 0.7 dpm kg^{-1} H_2O! Current and past decade rains have tritium levels between 1.5 TU (tropics) and about 20 TU. There are large temporal and geographical variations.

A. Samples to be treated by full electrolytic enrichment (I.A.2), and expected to be above 30 TU (0.1 pCi mL^{-1}), are treated differently than those close to 0 TU. In order to preserve optimal accuracy, some preliminary information is desirable on these samples. Submitters of samples are therefore strongly advised to contact the laboratory in order that proper precautions may be taken. Uncontaminated rainwater for the last decade should be well below 30 TU.

B. For samples with expected activity above 1000 TU (3 pCi mL^{-1}) we must be given clear notice. Such "hot" samples would originate from the vicinity of nuclear installations. Direct gas counting (I.A.I) can accept samples up to 10,000 TU (32 pCi mL^{-1}), but such samples could easily be measured in a commercial-type liquid scintillation system and should not be sent to us.

NOTE: The submitter of a "hot" sample must bear any cost for loss of analytical capability due to the carry-over of tritium from the submitter's samples to other samples in our operation.

C. Chemically contaminated samples, in general, cannot be treated by electrolysis. Smaller amounts of non-volatile salts like sodium chloride, are allowable, as are low concentrations of hydrogen sulfide. These contaminants are removed by distillation in oxygen atmosphere and/or by addition of potassium permanganate. Not allowed are, in particular, organic matter, like light oils, alcohols, phenols, and volatile inorganics like arsenic compounds. Such chemicals will distill with the water and cause extensive damage to electrolysis and counting equipment. We reserve the right to refuse processing any samples that we judge to be too contaminated or `dirty' to run through our system. It is our experience that leachates from 'landfills' are frequently chemically contaminated, and also often have very high TU-values (>1000 TU), probably from medical waste and discarded watches with luminescent paint. However, in many cases we can perform Direct runs (see I.A.1) on such samples.

D. For his/her own benefit, a potential submitter is advised to contact the laboratory regarding procedures for field sampling and storage of ultra-low-level samples to avoid contamination in the field or during transport. In particular, a wristwatch with a luminescent dial is surrounded by a cloud of tritium water vapor! See the section `Advice on Sampling'.

TRITIUM PROCEDURES AND STANDARDS

1. LOW LEVEL ANALYSIS OF TRITIUM BY GAS PROPORTIONAL COUNTING.

All numbers of quantities, etc., are typical only and vary from sample to sample.

A. Distillation

300 mL of the water sample are distilled with continuous reflux to dryness or near dryness. During the procedure, the still is vented to the ambient air through a drying agent to avoid contamination of the sample by atmospheric water vapor.

B. Electrolytic Enrichment

The object of this procedure is to reduce the volume of the sample from 275 to 5 mL while preserving a large fraction of the tritium. The normal starting volume is 275 mL of which 75 mL are charged into the electrolytic enrichment cell. To that portion, 2 mL of concentrated sodium hydroxide solution (made from dead water and sodium peroxide or oxide) is added, and the remainder of the sample is transferred to a container on top of the cell. The sample is electrolyzed for 24 hours at 5 amps, current-regulated, which removes 50 mL of water. Once a day the solution in the cell is topped up from the container to the 75 mL mark, and the procedure is continued. When a total of between 20 and 50 mL of the sample remains, power is changed to constant voltage of 3.15 V, and later reduced to 2.75 V, until the process stops at the lower edge of the anode, leaving about 5g of enriched sample. This procedure takes 10 - 14 days, and the remaining amount of water typically contains 80% of the original amount of tritium. The enriched water sample is vacuum distilled from the sodium hydroxide, and the yield is weighed to ± 2 mg, and the value is adjusted for hydrogen left in the sodium hydroxide.

C. Preparation of Sampling Gas

About 3 mL of the enriched water sample is injected into a vacuum system. The water evaporates, and the vapor is reduced by hot magnesium metal to hydrogen gas which is absorbed on activated charcoal at liquid nitrogen temperature in a stainless steel pressure cylinder. Approximately 4 L atm of hydrogen is obtained this way.

D. Low-Level Counting

The low-level gas proportional counters have an active volume of 1 L and are shielded by 2.5 cm of selected lead, a ring of anti-coincidence Geiger counters, 10 cm of paraffin wax, boric acid and/or borated polyethylene, and at least 20 cm of iron, plus the walls and ceiling of the building. The counter is first filled with 10 psi (67 kPa) of propane. Thereafter, the sample hydrogen gas, under pressure in its cylinder, is added to the counter for a total pressure of 40 psi (300 kPa). The counter is then sealed off, and the gas amplification is set to specifications by adjusting working voltage using an external radioactive source. After that, counting proceeds until criteria for accuracy or sensitivity have been met. The pulses are sorted into several channels, of which some are used for continuous control of the gas amplification, as shown in the cosmic radiation spectrum, etc. Counting times are 6 to 20 hours. A 1 TU original sample enriched from 275 to 6 mL typically shows 0.6 cpm in the tritium channel above a background of 0.40 cpm, known to ± 0.02 cpm or better. The control of filling and counting procedures and calculation of results, as well as numerous checks on the performance of the machinery, are computerized. Software and hardware associated with this procedure are year 2000 compliant.

E. Backgrounds and Standard

At least once weekly each counter counts dead hydrogen gas (from petroleum). In addition, water from the deep Floridan Aquifer (more than 10,000 years old water) is reduced to occasionally check on the tank hydrogen gas. This procedure sets the background count of the counting equipment. Each batch of sodium hydroxide solution is also tested for blank value. A further check on process blanks is that at least once a week a sample of dead water (from the Floridan Aquifer) goes through all the same procedures, including enrichment, as the unknown samples. In order to check on the efficiency of the enrichment procedure, at least once a week a sample of known activity is processed through the entire system of enrichment, reduction, and counting. The efficiency of each counter is determined by counting hydrogen gas made by reduction of standard water in our regular preparation system. This standard water is prepared from NIST (formerly United States National Bureau of Standards) SRM #4926 by dilution by weighing. The dependence of background, efficiency, etc., on pressure, gas composition, gas amplification, etc., is known, and the appropriate corrections are applied via the software of the computing system.

F. Update

Periodically, usually about every six weeks, all measurements in all counters for the preceding time period are recomputed, applying statistical tests, and scrutinized for flaws in quality. This includes all measurements of unknowns, backgrounds, blanks, enrichment factors, efficiencies, etc. Only after this step is the result considered final. The results are then reported in Data Releases, one for each project or job.

G. Further Technical Information

The laboratory has successfully participated in all international low-level cross-check projects run by the International Atomic Energy Agency in Vienna. These projects are run approximately every five years. The procedures of tritium analysis are described in the following publications from this Laboratory, reprints furnished on request:

Östlund, H.G., H.G. Dorsey and C.G. Rooth, 1974. GEOSECS North Atlantic radiocarbon and tritium results, Earth Planet. Sci. Lett., 23, 69-86.

Östlund, H.G., M.O. Rinkel and C. Rooth, 1969. Tritium in the equatorial Atlantic current system, J. Geophys. Res., 74(18), 4535-4543.

Östlund H.G., Tritium, in GEOSECS Atlantic, Pacific, and Indian Ocean Expeditions, Vol. 7, Shorebased Data and Graphics, 7-10, 1987. (Describes procedures and examples of reliability tests. Reprints available from our laboratory.)

2. SAMPLE IDENTIFICATION AND FLOW OF INFORMATION

Water samples for tritium analysis are received and inventoried using the accompanying packing list or chain of custody supplied by the client. A computer worksheet listing sample name, volume, sample collection date, and date of arrival into lab, as well as client information, is generated. At this time, each order is given a unique job number, and each sample decimal numbered within that job. For example, the job-sample number (JB#), 123.05 indicates the fifth sample in the listing for job 123. The computer input is proofread, and the worksheet and labels are printed. An abbreviated copy of the worksheet listing is given to the administrative personnel to be filed with the client's records. The worksheet is used by the preparation technician to keep track of the progress of the samples. Preliminary results are recorded on this sheet as they become available through the computer. From the time the worksheet is printed, the sample is referred to by its JB#. Triple copy labels are attached to each sample bottle.

When processing begins, one of the labels bearing the JB# is attached to the processing vessel; the label then "follows" the sample through the preparation steps; i.e., it is physically transferred to the next process container. The same label is used from the beginning distillation through electrolytic enrichment, vacuum distillation and reduction to hydrogen gas and is eventually attached to the face of the pressure gauge of the counter in which the sample is counted. During each step of the process, a record is kept of the individual units of the preparation apparatus associated with the sample. A yellow preparation card reports the distillation date and unit #; electrolysis starting date; volume and cell #; and freeze-out date and unit #. Recorded also are the order number through the reduction system, and the cylinder # used to store the gas sample prior to counting.

When a sample is ready for activity measurement, the sample I.D. is merged with all the process information in the computer. Together, the data are entered into the particular sample file along with counter-fill data, sample pressure and temperature, a unique run number, and the time and date. Upon completion of the counting, temperature and pressure of the sample within the counter are again recorded for comparison and checked for computer input error. All records of the sample preparation information and counting results are stored in computer files. A listing of all samples prepared and counted the week before is printed every Monday to study for possible problems with the preparations and/or counting equipment.

Using these procedures, every sample can be easily traced from the moment it arrives in the lab to the final result.

ADVICE ON TRITIUM SAMPLING

SAMPLING OF ENVIRONMENTAL WATER FOR LOW LEVEL TRITIUM ANALYSIS

A. Explanation

Tritium in environmental samples will be determined with a limit of detection, of 0.1 T-units (TU) (0.3 pCi L^{-1}). Rains and water vapor of the open air varies from 2 to 30 TU. Indoors, the atmospheric humidity may reach 10,000 TU from various luminescent dials. Exposure of the water to such air at any temperature might give badly erroneous tritium results.

B. Sample bottles

In the past we recommended using 1 liter. (1 qt.) glass bottles with "PolySeal", caps for storage and shipping. With today's low tritium levels in outside air this may no longer be necessary. There have always been losses from bottles breaking during shipment. Except for extended storage (years) indoors, we now recommend the use of high density polyethylene bottles, such as U.S. Department of Transportation Spec DOT-2. The bottles should be clean and dry, preferably factory fresh. They must have good caps. Hold a filled bottle upside-down and squeeze hard. No leakage is allowed. Remember that there are large pressure changes in air transport. Pack in sturdy boxes with plenty of cushion material. Camping coolers make excellent shipping containers. (Note: we do not return them, ref II.7).

If you use glass, each bottle should be bubble-wrapped or placed in its own cardboard compartment within the container. Additional packing material such as shredded paper, more bubble-wrap or "peanuts" can be used to fill remaining space. Double boxing with packing in between is also encouraged. Ordinary coolers, used in place of cardboard boxes, provide an extra degree of protection.

If transfer is to be made indoors, the dry bottles should first be filled with argon gas. See below.

C. Sampling procedure

1. Sample transfer should be done outdoors, unless a specially vented room is available with ban on wristwatches.

2. THE PERSON PERFORMING THE SAMPLE TRANSFER IS NOT ALLOWED TO WEAR A WRISTWATCH, COMPASS OR SIMILAR WITH LUMINESCENT DIALS OR SO CALLED "BETA" LIGHTS.

3. Fill the bottle not quite to the neck with sample, leaving a few cm^3 of air. Do not rinse. Overflow is not desirable. Replace and screw cap on tightly.

4. Record bottle numbers on original field data sheets, and fill in information on bottle label.

5. If sampling must be made indoors, never let the water be exposed to the air. Pipe the sample water into the middle of an argon-filled bottle (below the argon level). Do not pour the argon out before, by tilting an open bottle.

6. Add nothing to the water sample. Avoid freezing which may crack the bottle.

GENERAL COMMENTS ON TRITIUM RESULTS

Tritium Scale (New Half-Life)

Tritium concentrations are expressed in TU, where 1 TU indicates a T/H abundance ratio of 10^{-18}. The values refer to the tritium scale recommended by U.S. National Institute of Science and Technology (NIST, formerly NBS), and International Atomic Energy Agency (IAEA). The TU-numbers are based on the NIST tritium water standard #4926E. Age corrections and conversions are made using the recommended half-life of 12.32 years, i.e., a decay rate of λ = 5.626 % $year^{-1}$. In this scale, 1 TU is equivalent to 7.151 dpm/kg H_2O, or 3.222 pCi/kg H_2O, or 0.1192 Bq/kg H_2O (Bq = disint/sec).

TU values are calculated for date of sample collection, REFDATE in the table, as provided by the submitter. If no such date is available, date of sample arrival at our laboratory is used. The stated errors, eTU, are one standard deviation (1 sigma) including all conceivable contributions. In the table, QUANT is quantity of sample received, and ELYS is the amount of water taken for electrolytic enrichment. DIR means direct run (no enrichment).

Remark: From 1 Jan 1994 through 31 Dec 2001 we used the previously recommended value for the half-life, 12.43 years. The use of the new number, 12.32 years, will in practice increase the reported TU-values by 0.9 %. This is insignificant since our reported values carry 1 sigma uncertainties of 3 %. It is interesting to note that through 1993 we used the older recommended value of 12.26 years.

Very low tritium values

In some cases, negative TU values are listed. Such numbers can occur because the net tritium count rate is, in principle the difference between the count rate of the sample and that of a tritium-free sample (background count or blank sample). Given a set of "unknown" samples with no tritium, the distribution of net results should become symmetrical around 0 TU. The negative values are reported as such for the benefit of allowing the user unbiased statistical treatment of sets of the data. For other applications, 0 TU should be used.

Reliability of results

Refer to Services Rendered (Tritium), Section II.8, in the "Tritium Laboratory Price Schedule; Procedures and Standards; Advice on Sampling". Tritium efficiencies and background values are different in the nine counters and values are corrected for cosmic intensity, gas pressure and other parameters. For tritium, the efficiency is typically 1.00 cpm per 100 TU (direct counting). At 50´ enrichment, the efficiency is equivalent to 1.00 cpm per 2 TU. The background is about 0.3 cpm, known to about ± 0.02 cpm. Our reported results include not only the Poisson statistics, but also other experimental uncertainties such as enrichment error, etc.

References

Lucus L.L. and M.P. Unterweger, Comprehensive review and critical evaluation of the half-life of tritium, J. Res. Natl. Inst. Stand. Technol., 105, 541-549, 2000.

Lucas, L.L., Massic activity ratios of the NBS/NIST tritiated-water standards issued between 1954-1999, J. Res. Natl. Inst. Stand. Technol., 105, 535-539, 2000.

CFC PROCEDURES AND STANDARDS

1. LOW LEVEL ANALYSIS OF CFC-11, CFC-12 AND CFC-113 BY PURGE-AND-TRAP GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION.

A. Sample Introduction

Samples are introduced into a 30 ml sample loop with a custom built apparatus that uses nitrogen to push the sample out from the bottom of the bottle.

B. Purge-and-Trap

CFC's are purged from the sample for 4 minutes with UHP N_2 flowing at a rate of 150 mL/min. The stream of nitrogen containing the CFC's is first passed over a trap containing magnesium perclorate (removes water vapor) and Ascarite (removes hydrogen sulfide, which can interfer with CFC-12). The dry, hydrogen sulfide free gas stream is then passed over a Porapak N trap held at -10°C which quanitatively removes the CFC's from the N_2 purge gas stream. After the 4 minute purge the main trap is isolated and electrically heated to 140° C to release the CFC's from the trapping material. Purging efficiency is checked by isolating a water sample in the purge chamber after it has been purged once and purging it a second time. Purging efficiencies are generally > 99 %.

C. Cryofocusing

Because of the relatively large amount of gas used to purge a sample, the CFCs spread out on the main trap as they are being purged from the water sample. If the CFCs were injected into the gas chromatograph (GC) directly from the main trap the resulting peaks would broad, diffuse and difficult to accurately quantify. Therefore the CFC's are transferred from the hot main trap to a smaller volume cryofocusing trap packed with Porapak N and held at -15^{o}C. The main to cryofocusing trap transfer is accomplished with UHP He flowing at 13 mL/min for 1 minute. This results in the CFC's being trapped on the cryofocusing trap in a nice tight plug.

D. Gas Chromatography

After the CFC's have been transferred to the cryofocusing trap, the trap is flashed heated electrically to 160 ^{o}C and the CFC's are transferred to the gas chromatographic column with UHP He flowing at 5 mL/min. The following chromatographic conditions are used. Column: 30 m x 0.32 mm GasPro capilliary column. Carrier Gas: He flowing at 5 mL/min, with the flow rate controlled using a mass flow controller. Column temperature: 90^{o}C for 1 min, then 10^{o}C/min to110 ^{o}C, then 15^{o}C/min to 170^{o}C, hold at 170^{o} C for 1 min. As the CFCs elute from the column they are detected using an electron capture detector. The limit of detection for this method is 0.010 picomoles/Kg for CFC-11, CFC-12 and CFC-113.

E. Standards and Blanks

Gas phase standards are prepared in our laboratory. The approximate concentration of CFC-11, CFC-12 and CFC-113 in these standards is 120, 270 and 80 picomoles of the respective CFC per mole of N_2 (parts-per-trillion). One standard containing all three compounds is used to construct a calibration curve by injecting different volumes of the standard. A fixed volume sample loop is loaded with the standard and the loaded sample loop is purged-and-trapped as described above. Various combinations of 5 different volume sample loops are used to construct a calibration curve consisting of at least 10 points. A calibration curve is run at least once a week. In order to ensure that the detector response to the CFCs remains stable with time, a single volume of standard is injected after every eight unknowns.

Standards containing such low CFC concentrations are not available from NIST, therefore the standards prepared in our laboratory are calibrated against standards obtained from the Scripps Institution of Oceanography and National Oceanographic and Atmospheric Administration's Climate Monitoring and Diagnostics Laboratory. Groups at these two laboratories maintain the currently accepted absolute calibration scales used in monitoring background atmospheric levels of CFCs. These two absolute calibration scales agree to within 2 % of each other.

System blanks are determined by loading the water sample loop with UHP N_2, and then purging-and-trapping the N_2 as described above. A blank is run after every eight unknowns. Blanks generally contain undetectable amounts of CFCs.

F. Update

Periodically, usually about every six weeks, all measurements for the preceding time period are recomputed, applying statistical tests, and scrutinized for flaws in quality. This includes all measurements of unknowns, blanks, purging efficiencies, standards, etc. Only after this step is the result considered final. The results, which include CFC concentrations and derived recharge ages, are then reported in Data Releases, one for each project or job.

G. Further Technical Information

Happell J.D. and D.W.R. Wallace, Gravimetric preparation of gas phase standards containing volatile halogenated compounds for oceanographic applications, Deep Sea Res., 44, 1725-1738, 1997.

Happell J. D., D. W. R. Wallace, K. D. Wills, R.J. Wilke, and C.C. Neill, A purge-and-trap capillary column gas chromatographic method for the measurement of halocarbons in water and air Rep. BNL-63227, 19 pp., Brookhaven National Laboratory, Upton, NY, 1996.

Happell J.D., and D.W.R. Wallace, Removal of atmospheric CCl_4 under bulk aerobic conditions in groundwater and soils, Environ. Sci. Technol., 32, 1244-1252, 1998.

Ekwurzel, B., P. Schlosser, W.M. Smethie, L.N. Plummer, E. Busenberg, R.L. Michel, R. Weppernig, and M. Shute, Dating of shallow groundwater: Comparison of the transient tracers $^3H/^3He$, chlorofluorocarbons, and ^{85}Kr, Water Resources Research, 30, 1693-1708, 1994.

2. SAMPLE IDENTIFICATION AND FLOW OF INFORMATION

Water samples for CFC analysis are received and inventoried using the accompanying packing list or chain of custody supplied by the client. A computer worksheet listing sample name, volume or weight, syringe or ampule number, salinity, temperature, sample collection date, and date of arrival into lab, as well as client information, is generated. At this time, each order is given a unique job number, and each sample decimal numbered within that job. For example, the job-sample number (CFC#), 123.05 indicates the fifth sample in the listing for job 123. The computer input is proofread, and the worksheet and labels are printed. An abbreviated copy of the worksheet listing is given to the administrative personnel to be filed with the client's records. The worksheet is used by the preparation technician to keep track of the progress of the samples. Preliminary results are recorded on this sheet as they become available through the computer. From the time the worksheet is printed, the sample is referred to by its CFC#. Labels are attached to each sample container. Once the sample is ready to be analyzed the CFC# and all other sample information is entered into the computer that controls the gas chromatograph and collects the raw data. After the sample is analyzed the computer controlling the gas chromatograph generates a database which includes all of the entered sample information along with the raw CFC peak areas. This data base also contains the information needed to calculate calibration curves and blank and efficiency corrections.

Using these procedures, every sample can be easily traced from the moment it arrives in the lab to the final result.

ADVICE ON CFC SAMPLING

SAMPLING OF ENVIRONMENTAL WATER FOR LOW LEVEL CFC ANALYSIS

A. Acceptable Methods of Drawing Water from Wells

Samples must be pumped from wells. Bailers will give unacceptable results because the groundwater sample will come in contact with air and will be contaminated by CFCs that are in the air. For example, if the sample was recharged 30 years ago when CFC concentrations in the atmosphere were much lower than present and it is exposed to present day air the CFC concentration in the sample will increase and the sample will appear younger than its actual recharge age.

Most plastic materials will also contaminate a water sample because small amounts of plastizers will leach into the water sample. The easiest type of pump to use is a peristaltic pump. In this type of pump only the pump tubing comes in contact with the sample. We have tested many different types of peristaltic pump tubing and have found that Viton tubing is the only type of material that will not contaminate the sample. Commonly used pump tubing materials, such as silicone or Tygon will seriously contaminate the sample. If a peristaltic pump with Viton tubing is not available, the Tritium Laboratory will arrange a loan of one of our pumps (client pays for shipping of the pump). Other types of pumps that have been used to successfully sample for CFCs are Bennett Pumps using copper tubing and Grunfos Rediflow 2 Pumps using polyethylene tubing. Also avoid the use of any type of lubricants, such as oils, greases, or sprays. Even small amounts of these materials will contaminate a sample. Insect repellent is another potential source of contamination.

B. Collection of Water for Low-Level CFC Analysis Using Bottles and Foil Lined caps.

This method was developed by the USGS Reston Chlorofluorocarbon Laboratory. Please see http://water.usgs.gov/lab/cfc/sampling/bottles/ for more information.

Source of bottles and caps

Bottles and caps can be obtained from the SKS bottle company on the internet at URL www.sks-bottle.com The bottles are 125ml (4 oz) boston round clear glass and have a cap size 22-400.

Item No. 40000040.01S is a case of 160 bottles with no caps.

Bottles are also available from any Wheaton glass supplier as Wheaton part number 217112, which is a case of 24 bottles with no caps.

The caps are sold as SKS item no. 6021-03, white metal caps with aluminum foil liner in a bag of 144. **USE ONLY THESE ALUMINUM LINED CAPS! THIS CAP IS THE KEY TO THE METHOD. Discard any caps, if the foil liner appears scratched, dented, or altered in any way.**

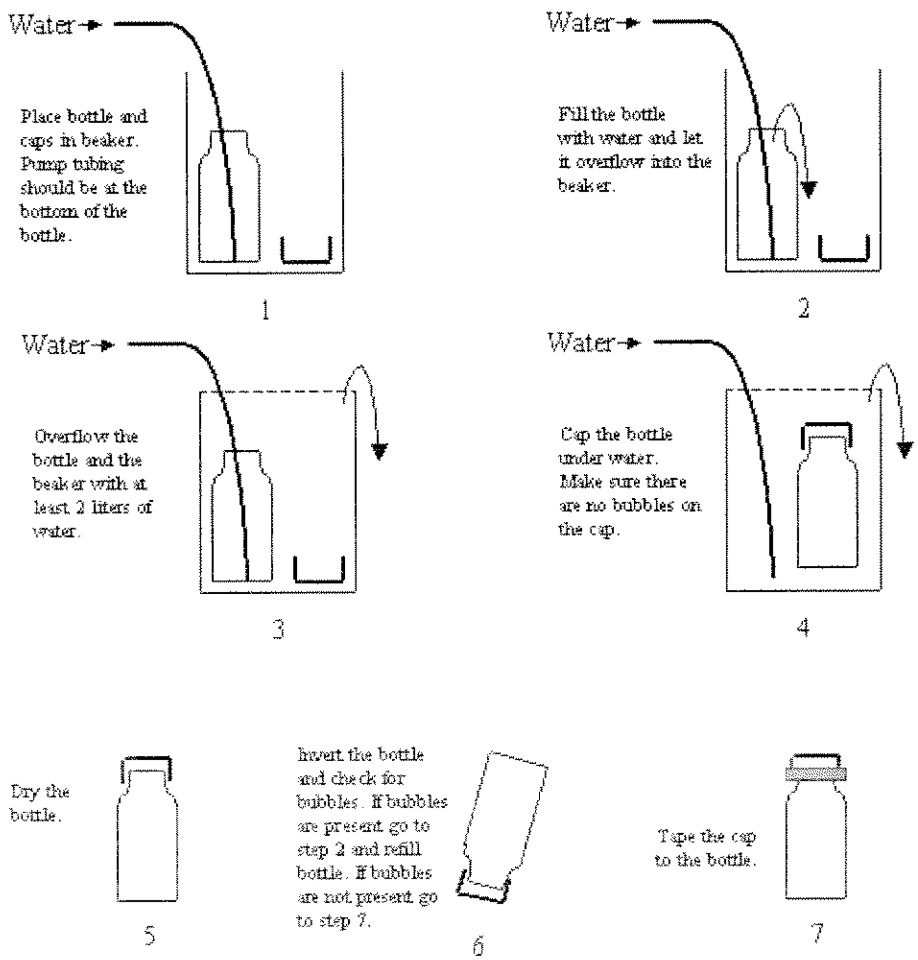
Filling procedure

The bottles and caps should be THOROUGHLY rinsed with the water to be sampled. The bottles are filled and capped underwater in a beaker. Refrigeration-grade copper, polyethylene, polypropylene, viton or polyurethane pump tubing is required. Soft flexible tubing, such as tygon or silicone tubing will almost certainly contaminate the sample. The filling procedure is carried out within a two to four liter beaker. A plastic beaker or bucket is fine. Fill a minimum of 3 bottles per sample.

The procedure is shown below and is as follows (refer to the figure below):

1. After the well has been purged, place the bottle in the beaker and then insert the end of the tubing from the pump all the way into the bottom of the bottle. Also place all the caps (2 or more) in the beaker.
2. Fill the bottle as shown with water until it overflows.
3. Continue to overflow the bottle until the beaker also overflows. Allow at least 2 liters of water to flow through the bottle and out of the beaker.
4. Select a cap from the bottom of the beaker and tap it under water to dislodge air bubbles. Remove the pump tube from the bottle and cap the bottle TIGHTLY underwater without allowing the water in the bottle to come in contact with air. Flushing the bottle with more water is far better than with less water.
5. Remove the bottle from the beaker and dry the bottle.
6. Invert the bottle, tap it and check it for air bubbles. If there are bubbles, repeat the procedure from step 2 above. **If it is necessary to refill the bottle, you must use a new cap.**
7. If there are no bubbles present, securely tape the cap to the bottle with electrical tape. Wrap the tape in a clockwise direction looking down at the bottle top. Do not forget to label each bottle with the well name, date, and time of sampling and the sequence number of each bottle as it was collected (i.e. 1, 2, etc).

USE ONLY THE METAL BOTTLE CAPS DESCRIBED IN THE TEXT ABOVE



Because the entire contents of each sample must be used for the analysis, it is recommended that you take duplicate or triplicate samples from each source. This will provide backups in case one of the samples is lost during shipping or during the analytical procedure. We will typically analyze the duplicate or triplicate samples and provide the results to the submitter at no additional cost.

GENERAL COMMENTS ON CFC RESULTS

A. CFC-Derived Recharge Age Calculation

Once the sample has been analyzed and the concentrations of CFC-11, CFC-12 and CFC-113 in the water sample have been determined the recharged age is calculated as follows:

1. Using the temperature dependent solubility function and the measured CFC concentration in the water, an "equivalent atmospheric concentration" for each CFC is calculated using the following equation:

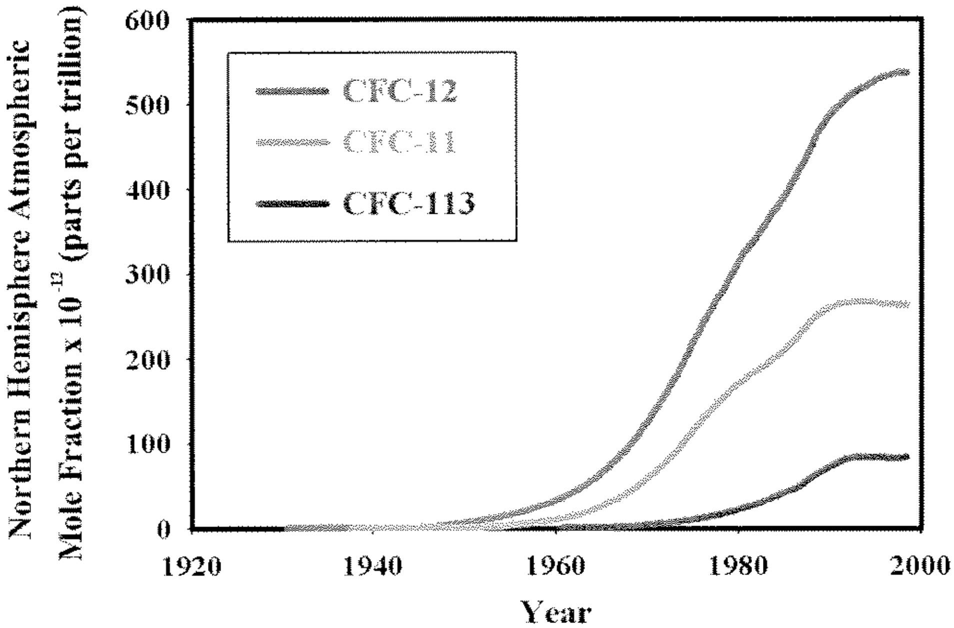
$$C_{EA} = C_W/F$$

where C_W = measured CFC concentration in the water sample, F is the temperature dependent solubility constant, and C_{EA} is the equivalent atmospheric concentration.

2. The equivalent atmospheric concentration for each compound is then compared to a plot of atmospheric CFC concentration versus time (see figure 1) to determine the year in which the sample was recharged.

3. The derived recharged age for each compound is then calculated by subtracting the year of recharge from the sampling date. The recharge ages derived from each compound are then compared to each other. If no problems are detected (see section D below) the ages derived from each compound are averaged to determine the CFC-derived recharge age.

Figure 1
Atmospheric History of CFCs



B. Recharge Temperature and Other Parameters

Because the solubility of the CFCs is dependent on temperature, an estimate of the recharge temperature (temperature of the water as it enters the aquifer) must be provided. Final CFC eqilibration usually occurs as rainwater is percolating through the unsaturated zone. The temperature of the unsaturated zone, for unsaturated zones < 30 m thick, is usually very close to the mean annual air temperature of the local area. Therefore the mean annual air temperature is usually a good estimate of the recharge temperature, if recharge is occurring locally. If the water sample is taken from a surfacial aquifer the measured water temperature is a good approximation of the recharge temperature. Recharge temperature may also be determined by measuring dissolved helium and neon in the groundwater (Noble Gas Laboratory) and calculating the temperature based on the helium and neon solubility functions. Please provide an estimate of the recharge temperature when sending samples. Because CFC concentrations in the water sample are reported in picomoles of CFC per kg of water, the salinity (or conductivity) of the water is also needed if sending samples by syringe. Please also provide dissolved oxygen and dissolved hydrogen sulfide concentrations, if these data are available.

C. Solvent Contaminated Aquifers

If the aquifer being sampled is known to be contaminated with solvents then the CFC concentations will almost always be supersaturated with respect to the highest atmospheric CFC concentration, or there will be many interfering peaks in the chromatogram which make accurate CFC quantification diffucult. Therefore, in most solvent contaminated aquifers, CFCs will not give valid recharge ages. Keep in mind that the maximum CFC-11, CFC-12 or CFC-113 concentration expected, if the atmosphere is the only source of CFCs to the aquifer, is ~ **10,000 times lower** than the drinking water standards for these compounds. Therefore, even if drinking water standards are met, the CFCs may still be supersaturated with respect to the highest atmospheric CFC concentration. Another way to think about this is that the edges of a solvent-contaminated plume of groundwater extend beyond the boundaries set by drinking water standards. If you expect that the groundwater you are sampling is contaminated with solvents, then the $^3H/^3He$ method (Noble Gas Laboratory) of deriving recharge age may be more appropriate. You will be charged for the analysis even if the CFC concentrations are greater than can be expected from equilibration with the atmosphere.

D. Potential Problems

CFC-11 is known to be degraded under anoxic conditions, and anoxic groundwaters will frequently have CFC-11 derived recharge ages that are older the CFC-12 derived recharge ages. CFC-113 was commonly used as a solvent in the electronics industry and can be found as a contaminant in some groundwaters. The atmospheric concentrations of CFC-11 and CFC-113 have leveled out or started to decrease in the recent past, which makes their input functions non-unique (i.e. for some CFC-11 and CFC-113 concentrations there will be two possible ages). CFC-12 does not suffer from any of these problems. It is not known to degrade under anoxic conditions. Although the rate of increase in the atmospheric concentration of CFC-12 has decreased in recent years its concentration it still slowly increasing. Its low boiling point (~ -50°C) precludes its use as a solvent, although CFC-12 contamination of an aquifer is possible. Some possible sources of CFC-12 contamination include, buried refrigerators, buried air conditioners, or heat-pumps which may leak CFC-12 into the groundwater that is commonly used as a heat sink in these devices.

E. References

Warner, M.J. and R.F. Weiss, Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, Deep-Sea Res., 32, 1485-1497, 1985.

Bu, X. and M.J. Warner, Solubility of chlorofluorocarbon 113 in water and seawater, Deep-Sea Res. I, 42, 1151-1161, 1995.

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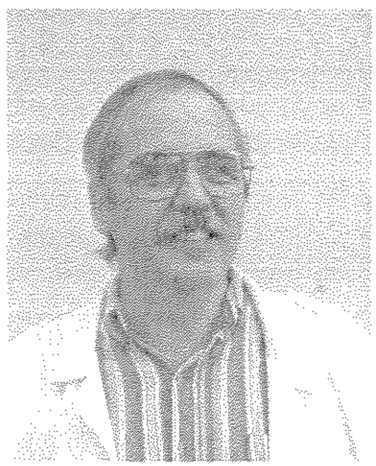

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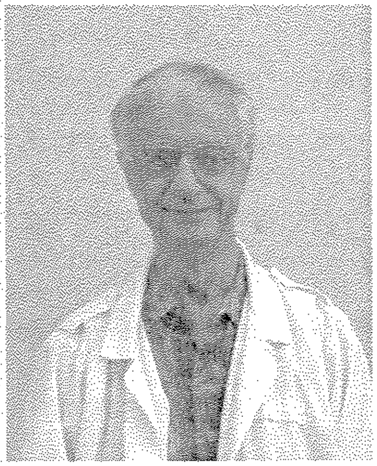

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ATTACHMENT D-5

TEST AMERICA (FORMERLY STL) VALPARAISO

STANDARD OPERATING PROCEDURE

Microbiology: Escherichia coli in Drinking Water

SEVERN TRENT STL

MICROBIOLOGY: Escherichia coli in Drinking Water

Written / Updated by:	***Signature***	***Date***
Michele Traina Microbiologist	Michele Traina	2/1/2006

Approvals:	***Signature***	***Date***
Chris Hoham Env. Health & Safety Coor.		2/1/2006
Ken Busch Quality Manager	Ken Busch	2/1/2006

CONTROLLED DOCUMENT DISTRIBUTION

COPY # : **UNCONTROLLED**

ISSUED TO :

Table of Contents

1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the procedure used to determine Escherichia coli in Drinking Water by the Readycult Method 9223B Version 13, dated November 2002.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not Applicable.

1.1.2 Reporting Limits

The reporting limit for this parameter is '**Present**' or '**Absent**'.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM, Revision 1).

1.2 Summary of Method

A substrate powder is added to a measured volume of aqueous sample. The substrate powder is for a 100 mL sample which is then shaken and incubated at 35.0 + 0.5°C for 24 hours. Any color change to blue-green confirms the presence of total coliforms. If the sample fluorescences, Escherichia coli is present. The results are reported as present/absent per 100mL.

2.0 INTERFERENCES

- Interference in this method is primarily caused by non-sterile sampling or testing conditions.
- Chlorine can interfere; and is removed by adding sodium thiosulfate to the sample container.
- Sterile conditions must be maintained at all stages for the successful analysis of coliform bacteria. Extensive guidance on microbiological drinking water regulations, quality assurance, equipment specifications, sterilization procedures, preparation of culture media and reagents, and sample collection, preservation, and storage is provided in Standard Methods'. Analysts performing microbiological analyses should refer to these sections for guidance.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Safety Concerns or Requirements

Work areas must be cleaned with bleach or disinfectant on a regular basis to prevent contamination.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: **This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Isopropanol	Flammable	400 ppm-TWA	Flammable liquid and vapor. Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Affects central nervous system. May be harmful if absorbed through skin. May cause irritation to skin.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Supplies

- Thermometers – Capable of reading in increments of 0.5°C or less; Calibrated using a NIST factory traceable thermometer.
- Fluorescent Light Source: Model UVL - 56
- Autoclavable Indicating Tape and Indicating Vials
- Autoclavable Waste Bags
- Aluminum Foil

4.2 Instrumentation

- Incubator - 35.0 +/- 0.5°C and it must maintain relative humidity.
- Autoclave (Market Forge): Capable of reaching and maintaining 121°C. Must reach and maintain 121°C during sterilization and require no more than 45 minutes for a complete cycle during a 12-15 minute sterilization period. The autoclave must depressurize slowly to ensure that the media does not boil or bubbles do not form in the fermentation vials.
- Refrigerator - Must maintain a temperature of 1-5°C; this thermometer is graduated in 1°C increments or less.

5.0 REAGENTS AND STANDARDS

5.1 Media

Readycult Coliforms 100. Contents: 20 tests (snap pack format).
One snap pack is sufficient for a 100 ml water sample.
EPA approved (40 CFR Part 141)

Life of Media: 36 months from the date of manufacture. See packaging for expiration date.
Storage Requirements: Store dry and tightly closed at 15 – 25°C.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control (QC) Checks

7.1.1 Performance Evaluation (PE) Sample

The laboratory should analyze one unknown PE sample annually provided by the ISDH, USEPA, or designated testing organization and report the results to ISDH.

7.1.2 Monthly Quality Control of Readycult test using test strains.

Test strains include Escherichia coli ATCC 11775, Citrobactor freundii ATCC 8090, and Salmonella typhimurium ATCC 14028.

The Quality Control procedure should be performed on each new lot number of Readycult packets or monthly. Read and record the results in a bound logbook.

- The EC bottle (Escherichia coli) should be green (present for total coliform) and fluorescent (present for E. coli).
- The CF bottle (Citrobactor freundii) should be green and not fluorescent.
- The ST bottle (Salmonella typhimurium) should be clear and not fluorescent.

If the results are not as above, the Readycult reagent should not be used and discarded.

7.1.3 Laboratory Environment

The laboratory must be clean, and temperature and humidity controlled. The working area must have adequate lighting (1000 LUX), water, gas, electrical outlets available as necessary to accommodate test procedures, 150-200 square feet, and 5-6 linear feet per analyst. The microbiological laboratory facilities must be separated from other areas of the lab.

7.1.4 Laboratory Sterilization

- The minimal autoclave time for contaminated materials and tests is 121°C for 30 minutes.
- Timing for sterilization begins when autoclave reaches 121°C.
- All equipment required to be sterilized must be wrapped in aluminum foil prior to
- autoclaving.
- Sterility checks must be performed on each lot of commercial and each batch of laboratory prepared materials used to contain, transfer, or inoculate water samples or sterile media. This includes all culture dishes, cotton swabs, pipettes, culture tubes and containers, glassware, and plastic ware.
- The countertop is wiped down with alcohol before and after sample analysis.

7.2 Sample Preservation, Holding Time and Storage

7.2.1 Sample Containers

The sterility must be checked by selecting one random container from each lot of commercial or each batch of laboratory prepared sample containers. The container is checked by adding 25 mL of single strength nutrient broth and incubated at 35.0 +/- 0.5°C for 24 hours. The container is then checked for growth by observing any cloudiness. If cloudiness is observed, the entire batch or lot number of containers must not be used for sampling and will be discarded.

The sample containers (supplied by STL) are non-fluorescent, transparent, sterilized vessels purchased from IDEXX or VWR. They have sodium thiosulfate added and are sterile 125 mL bottles. A random container needs to have the auto fluorescence checked prior to distribution by shining a fluorescent light upon the unused container (refer to the previous paragraph).

A minimum volume of 100 mLs should be collected. The sample should be controlled at 1-5°C during transportation. The recommended transportation time is 6 hours. The sample is then refrigerated upon arrival. Sample analysis must be completed within 6 hours after sample receipt if stored at room temperature or within 24 hours if stored in the refrigerator.

Analysis must be done within 30 hours of collection time.

7.3 Sample Preparation

Not Applicable.

7.4 Calibration / Standardization

Not Applicable.

7.5 Preventive Maintenance

- The incubators must be professionally serviced annually and written in a bound logbook.
- The autoclave must be professionally serviced annually and written in a bound logbook. The temperature gauge must be calibrated and tagged annually.
- Check the autoclave sterilization temperature weekly using a maximum registering thermometer (MRT) (90-200°C) and recording in a bound logbook.
- Check the automatic timing mechanism with a stop watch monthly. Record in a bound logbook the times for both the automatic timing mechanism and the stopwatch. The timing for sterilization begins when the autoclave reaches 121°C. Heat sensitive tape, spore strips or spore ampoules are used during each sterilization.
- Clean the refrigerator at least once per month. Throw away all out dated materials. No food or drink is allowed in this refrigerator.
- The refrigerator must be professionally serviced annually and written in a bound logbook.

7.6 Sample Analysis

7.6.1 Label the 100 mL sample upon arrival. Be careful to allow ample open area on the collection container to determine results. This means sample labels should not cover the entire bottle. The sample is placed in a refrigerator at 1-5°C upon arrival. The sample stays in the refrigerator until analyzed.

7.6.2 The chain of custody (COC) must have filled out: the client information, billing information, sample number, sample description, sample date and time, matrix, sample container, number of samples, method required, sampler's signature, client's signature, person relinquishing the samples signature, date and time, and the person receiving the samples signature date and time.

7.6.3 The chain of custody should then be checked to verify what was written on the sample container and what method and information was entered in the computer. Check LabNet (a.k.a., the LIMS) for the correct test method.

7.6.4 The bench top is disinfected by applying a volume of isopropyl and wiping down the entire counter top with a paper towel.

7.6.5 Take one snap pack, lightly tap to ensure the granules are at the bottom. Bend the upper portion of the snap pack until it breaks open. Do not touch the opening to avoid contamination!

7.6.6 Add the contents to a 100 mL. water sample in a sterile, transparent non-fluorescing vessel with a minimum capacity of 120 mL.

7.6.7 Shake the capped vessel to dissolve granules completely.

7.6.8 Incubation: 18-24 hours at 35 to 37°C. If incubation is at room temperature (20 to 25°C) the incubation time is prolonged to 48 hours. Incubation at room temperature can be used as a back –up method in case of power failure.

7.7 Documentation

- Record in a bound logbook the identification of each thermometer, the temperatures displayed on the certified thermometer and the thermometer being certified, name of the analyst and dates the quality control checks were done, and correction factors.
- Incubators: The temperatures must be recorded in a bound logbook twice per day with readings separated by at least four hours. In this same logbook, record the days the incubator is in use.
- Record in a bound logbook each Autoclave sterilization cycle. Include the autoclave contents, date, time-in and time-out, time at sterilization temperature, total time autoclaved, and maximum temperature attained.
- Refrigerator temperature is recorded daily in a bound logbook using a calibrated thermometer immersed in liquid. Record in this logbook the days the refrigerator is in use.

7.7.1 Analysis Logbook and Data Reporting

All raw data must be entered as it is acquired in the designated bound logbook. This includes test method, analyte being determined, analyst's initials, and date of test. All information and data which are pertinent to the test should be recorded to facilitate data validation. Any unusual conditions, information on the appearance of the samples, or any other factors which may influence the results should be noted in the bound logbook.

The analyst must enter the date and time of analysis for each batch of samples processed. Enter the date and time that the procedure was initiated.

The runlog must be completed for each days analysis.

Associated Documents and Forms

- Incubator 1 Temperature Bench sheet
- Incubator 2 Temperature Bench sheet
- Refrigerator Temperature Bench sheet

- Water Bath Temperature Bench sheet
- Laboratory Pure Water Monthly Record
- Readycult Monthly Check
- Thermometer Calibration
- Autoclave Information Sheet
- Monthly Autoclave Check List
- Supply Log
- Media Log
- Equipment Service Records

7.7.2 Traceability of Standards

Upon receipt, the media is assigned a unique ID# based on the lot number, date of receipt, and the date of expiration. A label with this ID# and the media's expiration date is placed on the container. This information is also documented in the QC log for the microbiology lab.

7.7.3 Data Review

All data has a secondary peer review prior to reporting. This is documented in the logbook by the signature/date of the reviewer. The analyst enters all data into LabNet and a secondary reviewer will report the results (i.e., update them into LabNet for reporting to the client). The data is additional noted in LabNet as being reviewed.

8.0 QUALITY CONTROL

8.1 QC Summary

The quality control data (Section 7.1) is not reported with the samples. It is entered in bound logbooks when performed.

8.2 Corrective Actions

- The incubator must not be out of temperature for more than two days in a row. If it is out of temperature, a service man must be called to fix the temperature of the incubator. The incubator must not be used until it is serviced and all samples must be removed.
- The refrigerator must not be out of temperature for more than two days in a row. If it is out of temperature, a service man must be called to fix the temperature of the refrigerator. The refrigerator must not be used until it is serviced. All media or samples must be removed.

9.0 Data Analysis and Calculations

No Color Change: (the broth remains yellowish in color): absence of coliforms and E.coli.

Total Coliforms:
Any color change of the broth to blue-green, even if only in the upper section, confirms the presence of total coliforms (X-GAL reaction)

E.coli:
Look for the fluorescence in blue-green colored vessels using UV light (365nm) in front of vessel (towards the sample and away from eyes). A bluish fluorescence indicates presence of E. coli (MUG reaction).

10.0 Waste Management and Pollution Control

Solid waste is autoclaved prior to disposal. Aqueous waste is dumped to sanitary sewer and is not autoclaved.

11.0 Method Performance Criteria

Refer to Sections 1, 6, 7 and 8.

12.0 References

Refer to Section 1.0

13.0 Attachments

Not Applicable.

Historical File:
Revision 1: 04/23/04
Revision 2: 12/19/05

Revision 2:
- Added table of contents.

ATTACHMENT E

ENSR DATA VALIDATION PROTOCOLS

ATTACHMENT E-1

INORGANIC DATA VALIDATION PROTOCOLS

DATA REVIEW WORKSHEETS

Type of Validation Full: ____
Limited: ____

ENSR Data Pkg#: ____________
Site Name: ____________
Project Number: ____________

REVIEW OF METALS ANALYSIS DATA PACKAGE

The following guidelines for evaluating metals were created to delineate required validation actions. This document will assist the reviewer in using professional judgement to make more informed decisions and in better serving the needs of the data users. Quality control validation criteria were derived from USEPA publications: "Test Methods for Evaluating Solid Waste, Physical / Chemical Methods SW846" (3RD Edition and subsequent Updates), specifically SW-846 methods 6010B, 7470A, and 7471A. Validation actions were derived from "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (Final, October 2004) and were modified to accommodate the non-CLP methods and professional judgment. The project QAPP should be reviewed for project-specific information.

The hardcopy data package received from (laboratory name/location) ____________ has been reviewed and the quality assurance and performance data summarized.

The data review for metals included:
Lab Project/SDG No. ________ No. of Samples: ________ Sample Matrix: ________
Field Blank IDs: ____________
Equipment Blank IDs.: ____________
Field Duplicate IDs.: ____________

The general criteria used to determine the performance were based on an examination of (check all that apply):

_____ Data Completeness
_____ Holding Times and Sample Preservation
_____ Calibrations
_____ Blanks
_____ ICP Interference Check Sample
_____ Matrix Spike Results
_____ Laboratory Duplicate Results
_____ Field Duplicate Results
_____ Laboratory Control Sample
_____ ICP Serial Dilution Results
_____ Sample Quantitation Assessment
_____ GFAA Results (Addendum)

NOTE: If GFAA methods (SW-846 7000 series) were used to analyze samples, the data validation of these analyses should be attached as an addendum to these Data Review Worksheets.

If spreadsheets are used to automate calculations, they must be attached to these worksheets.

Overall Comments: ____________

____

Definitions and Qualifiers:
J - Estimated result with undetermined bias
J+ - Estimated result, result may be biased high
J- - Estimated result, result may be biased low
QL – quantitation limit (the laboratory may use reporting limit, practical quantitation limit, detection limit)
U - analyte not detected
UJ - Estimated nondetect – quantitation limit is estimated
R - Rejected data (unusable)
MDL or IDL – Method detection limit or instrument detection limit, respectively

Actions based on MS, laboratory duplicate, field duplicate, serial dilution analyses should be applied to all samples of the same matrix or to the results of all samples within a given area of the site, if deemed appropriate. Any validation action based upon professional judgement or any deviation from the validation guidelines presented in these worksheets needs to be described in detail in an attached narrative or memo.

Reviewer: ____________ Date: ____________

All criteria were met: ____
Criteria were not met,
and/or see below: ____

I. DATA COMPLETENESS

A. Data Package:

_______ The tests requested on the COC or in subsequent communications were performed and reported.

_______ The correct analyte list was reported.

_______ The COCs (external and internal) are present and complete.

_______ Sample receiving documentation is complete.

Missing Information	Date Lab Contacted	Date Received

B. Other Discrepancies

All criteria were met: ____
Criteria were not met,
and/or see below: ____

II. HOLDING TIMES (HT) and SAMPLE PRESERVATION

The objective of this parameter is to ascertain the validity of results based on the sample condition, and holding time of the sample from the time of collection to the time of preparation, and subsequently from the time of preparation to the time of analysis. Complete the table for all samples and circle the analysis date for samples not within criteria.

Sample ID	Date Sampled	Mercury (Hg) 7470A/7471A Date Analyzed	Metals by ICP 6010B Date Analyzed	pH	ACTION

Cooler temperatures: ______________________

Criteria (professional judgement):

- Analysis HT: Mercury – 28 days from sample collection; Other metals - 180 days from sample collection
- Aqueous Preservation: pH $\leq$ 2 with nitric acid for all metals.
- Cooler/Storage Temperature: 4°C $\pm$ 2°C for aqueous and solid matrices until preparation and analysis

Actions (to be used as professional judgement):

1. If aqueous samples were not properly preserved in the field or upon receipt (within 24 hours of sample collection) or if samples were not digested within 24 hours, qualify detected results as estimated low (J-) and reject nondetects (R).
2. If holding times are exceeded, qualify detected results as estimated low (J-) and reject nondetects (R).
3. If HTs are grossly exceeded (> 2x), notify the Project Chemist for action.
4. If samples were not at the proper temperature (>10°C), the validator should document all justifications for qualifying or not qualifying sample data in the validation memo. For example, SW-846 only requires thermal preservation for mercury in soils.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

III. INSTRUMENT CALIBRATION

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrumentation is capable of producing and maintaining acceptable quantitative data.

1. Analytical Sequence

A. Did the laboratory use the proper number of standards for calibration as described in the method or per manufacturer's recommendation? (ICP metals = a blank and at least one standard, Hg = a blank and at least five standards) — Yes or No

B. Were initial calibrations performed successfully on a daily basis or once/24 hours and each time the instrument was set up? — Yes or No

C. Were all measurements the average of at least two replicate exposures? — Yes or No

D. Was an initial calibration verification standard (ICV) analyzed for all analytes at the proper concentration (e.g., within the linear range for 6010B) and at the beginning of sample analysis? — Yes or No

Was the ICV made from a second source (different than calibration standards)? — Yes or No

E. Were continuing calibration verification standards (CCVs) analyzed for all analytes immediately following daily calibration, every 10 samples, and at the end of the run at a mid-range concentration? — Yes or No

F. Although not required by SW-846, if a Contract Required Quantitation Limit (CRQL) check standard was analyzed, was the concentration of this CRQL standard at or comparable to the QL reported by the laboratory? — Yes or No
Note: for ICP analysis, the CRQL check standard is often referred to as CRI standard. For CVAA, the CRQL check standard is often referred to as CRA

Actions:

1. If the calibration was not performed, qualify all results as unusable (R).
2. If the calibration is incomplete or if any of the above answers are "No", data quality may be affected.

Use professional judgment to determine the severity of the effect. Discuss any actions below and list the samples affected.

____
____
____
____
____

All criteria were met: ____
Criteria were not met,
and/or see below: ____

III. INSTRUMENT CALIBRATION (continued)

2. Recovery Criteria

List the analytes which did not meet the percent recovery (%R) criteria for the ICV, CCV, CRI, or CRA.

Date	ICV, CCV CRI, or CRA	Analyte	%R	Action	Samples Affected

Criteria:

Calibration standard	**%R**	**CRI/CRA standard**	**%R**
ICP Metals ICV or CCV	100 ± 10	ICP Metals (except Sb, Pb, Tl) CRI	100 ± 30
Mercury ICV	100 ± 10	Sb, Pb, Tl CRI	100 ± 50
Mercury CCV	100 ± 20	Mercury CRA	100 ± 30

Actions*: If any analyte does not meet the %R criteria, follow the actions stated below:

Full Validation:
1. For ICV nonconformance, apply action to all samples in the analytical sequence.
2. For CCV nonconformance, apply action to samples analyzed between the previous in-control CCV and the subsequent in-control CCV.

* As stated in the NFGs, use professional judgement to qualify.

	%R of Analyte in the ICV/CCV and Recommended Actions				
ICP Metals ICV/CCV and Mercury (ICV)	**< 75%**	**75 to 89%**	**111 to 125%**	**126 to 160%**	**> 160%**
Mercury (CCV)	**< 65%**	**65 to 79%**	**121 to 135%**	**136 to 170%**	**> 170%**
Detected Results	J- or R	J-	J	J+ or R	R
Nondetects	R	UJ	A	A	A

Qualification based on CRI/CRA	**%R of Analyte in the CRI/CRA and Recommended Actions**			
ICP Metals (except Sb, Pb,Tl) and Mercury	< 50%	50 to 69%	130 to 180%	> 180%
Sb, Pb,Tl	**< 30%**	**30 to 49%**	**150 to 200%**	**> 200%**
Detected Results > 2X the CRI/CRA	J	A	A	R
Detected Results < 2X the CRI/CRA	R	J-	J+	R
Nondetects	R	UJ	A	A

All criteria were met: ____
Criteria were not met,
and/or see below: ____

IV. BLANK ANALYSIS RESULTS

The objective of blank analysis results assessment is to determine the existence and magnitude of contamination resulting from laboratory or field activities. The criteria for evaluation of blanks apply to any blank associated with the samples, (e.g., equipment blank [EB], field blank [FB], preparation blank [PB], initial and continuing calibration blanks [ICB/CCB], etc.). If problems with any blank exist, all data associated with the case must be carefully evaluated to determine if there is an inherent variability in the data for the case, or if the problem is an isolated occurrence not affecting samples.

A.	Was a PB analyzed for each matrix or with each batch of samples digested (≤ 20 samples)?	Yes or No
B.	Was an ICB analyzed after the calibration standards ?	Yes or No
C.	Was a CCB analyzed after ever ten samples and at the end of the run?	Yes or No

Data quality may be affected if any of the above answers are "No". Use professional judgment to determine if the associated sample data should be qualified. Discuss any actions on a separate attached shseet, and list the samples affected.

Actions

Blanks must be evaluated in the following order:

- Lab blanks (preparation and calibration) must first be used to qualify equipment/field blanks and samples.
- Any contamination remaining in the equipment/field blanks will be used to qualify the associated samples.

Full Validation:

1. For PB nonconformance, apply action to all samples in the analytical batch.
2. For ICB nonconformance, apply action to all samples in the analytical sequence.
3. For CCB nonconformance, apply action to samples analyzed between the previous in-control CCB and the subsequence in-control CCB.

Limited Validation: Use the highest blank PB, ICB, or CCB in the analytical batch or sequence.

The blank actions/qualifications on the following page are written for CLP methods and not SW-846. Therefore, professional judgment may be used to modify some of the actions (e.g., in the case where QLs are extremely high or not technically supported). It may be appropriate to use actions for blanks from the 1994 National Functional Guidelines (e.g., if the laboratory reports nondetects at the MDL/IDL). Justification for using this approach must be documented in the worksheets and in the validation memorandum.

The guidelines below should be followed when using the 1994 National Functional Guidelines and the "5x rule".

Establish an Action Level (AL) for any analyte equal to five times (5x) the highest concentration of that element's contamination in any blank. Any blank with a negative result whose absolute value > IDL or MDL (or lowest quantitation limit) must be carefully evaluated to determine its affect on the sample data. Use professional judgment to assess the data.

Blanks must be evaluated in the following order:

- Lab blanks (preparation and calibration) must first be used to qualify equip/field blanks and samples.
- Any contamination remaining in the equip/field blanks will be used to qualify the associated samples.

Actions:

1. For positive blank contamination:
   - results ≤ AL are qualified as undetected (U) at the reported concentration.
   - results > AL or nondetects are accepted unqualified.

2. For negative blank contamination:
   - results ≤ absolute value of negative AL are estimated (J).
   - nondetects are estimated (UJ).
   - results > AL are accepted unqualified.

3. When both positive and negative blank contaminations exist, use professional judgment to assess data.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

October 2004 National Functional Guidelines

Blank Actions

Blank Type	Blank Result	Sample Result	Action for Samples
ICB/CCB (Positive)	≥ MDL but ≤ QL	Nondetect	No action
		≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL	Use professional judgement (see below [1])
	>QL	≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL but < Blank Result	Qualify as nondetect (U) at the blank level Or qualify result as unusable (R).
		> Blank Result	Use professional judgement (see below [1])
ICB/CCB (Negative)	≤ (-MDL) but ≥ (-QL)	≥ MDL or nondetect	Use professional judgement (see below [2])
	< (-QL)	< 10x QL	Quality results ≥ QL as estimated low (J-) and nondetects as estimated (UJ)
		> 10x QL (professional judgment)	No action (professional judgment)
PB / EB / FB (Positive)	> QL	≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL but < 10x Blank Result	Qualify results as unusable (R) or estimated high (J+)
		≥ 10x Blank Result	No action
	≥ MDL but ≤ QL	Nondetect	No action
		≥ MDL but ≤ QL	Qualify as nondetect (U) at the QL
		> QL	Use professional judgement (see below [1])
PB (Negative)	< (-QL)	< 10x QL	Qualify results ≥ QL as estimated low (J-), non-detects as estimated (UJ)
		> 10x QL (professional judgment)	No action (professional judgment)

[1] Consider establishing an action level (AL) at 5x the blank contamination. If sample result is <AL, qualify the reported result with a "U".

[2] Consider estimating positive results and nondetects (J-/UJ).

All criteria were met: ____
Criteria were not met,
and/or see below: ____

IV. BLANK ANALYSIS RESULTS (continued)

Laboratory blanks

Matrix: Solid / Aqueous

Date Analyzed	Prep/ ICB/CCB	Analyte	Concentration (circle highest)	Units	Actions for Samples	Affected Samples

Field/Equipment blanks

Date Collected	Field ID	Analyte	Concentration	Units	Actions for Samples	Affected Samples

The blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples.
For example, soil sample results will not be in the same units as the ICB, CCB, EB, or FB data. It may be easier to work with the raw data or use the following equation to convert results in μg/L to mg/Kg.

ICB, CCB, EB, or FB concentration in μg/L must be converted to mg/kg in order to compare with sample results.

$$\text{Concentration in } \mu\text{g/L} \times \frac{\text{Volume diluted to (}\quad\text{ml)}}{\text{Weight digested (}\quad\text{g)}} \times \frac{1\text{L}}{1000\text{ml}} \times \frac{1000\text{ g}}{1\text{kg}} \times \frac{1\text{mg}}{1000\ \mu\text{g}} = \text{wet weight (mg/kg)}$$

For each sample, the concentrations are converted to dry weight using the % solids calculation:

$$\frac{\text{Wet weight conc}}{\text{\% Solids}} \times 100 = \text{Concentration in dry weight (mg/kg)}$$

All criteria were met: ____
Criteria were not met,
and/or see below: ____

V. ICP INTERFERENCE CHECK SAMPLE

The ICP interference check sample (ICS) verifies the analytical instrument's ability to overcome interferences typical of those found in samples and verifies the laboratory's interelement and background correction factors.

1. Frequency Requirements

A. Was the ICS solution analyzed at the beginning of each sample analysis run? Yes or No

If no, the data may be affected. Use professional judgement to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

____
____
____

B. Did the laboratory analyze an ICS A solution (not required in 6010B)? Yes or No

2. Recovery Criteria

List any elements in the ICS solution, which did not meet the %R criteria. Also evaluate the ICS A if the laboratory performed this analysis. Use professional judgment for actions or use those listed below.

Date	Analyte	%R	Action	Samples Affected

Criteria: %R = 100 ± 20% the true value or the true value ± 2x the RL (whichever is greater).

Actions: If any analyte does not meet the %R criteria, follow the actions stated below:

Full Validation: Use %R = 100 ± 20% and apply action to samples analyzed between the previous in-control ICS and the subsequent in-control ICS (if the ICS was analyzed more frequently than the method requirement) if samples contain interferents at levels comparable to or greater than the levels in the ICS.

Limited Validation: Use %R = 100 ± 20% and apply actions to all samples in the analytical sequence if samples contain interferents at levels comparable to or greater than the levels in the ICS..

Qualify results	**%R of Analyte in the ICS Solution**		
	%R < 50%	**%R = 50%-79% or < true value - 2x RL**	**%R > 120% or > true value + 2x RL**
Detected Results	J-	J-	J+
Nondetects	R	UJ	A

V. ICP INTERFERENCE CHECK SAMPLE (continued)

3. ICS A Analysis Results (using ENSR professional judgment and guidance from the NFGs since analysis of the ICS A solution is not required in 6010B)

List the concentration of any elements ≥ MDL (or lowest quantitation limit used) in the ICS A solution that should not be present. For soil samples, results might not be in the same units as the ICS solutions; it may be easier to work with the raw data.

List the samples affected by interferences below:

Interferent	Concentration in ICS A (ug/L)	Sample ID	Sample ID	Sample ID	Sample ID	Sample ID
Al						
Ca						
Fe						
Mg						
Element						

Criteria: No target analytes should be present in the ICS A solution at concentration ≥ MDL.

Actions:

1. If an element was detected ≥ MDL but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are < ICS A; accept results unqualified.

2. If an element was detected ≥ MDL but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are comparable or higher than those found in the ICS A, qualify detected results for the affected element as estimated biased high (J+) and accept nondetects.

3. If an element was detected as negative interference, (i.e., the absolute value ≥ MDL) but should not be present in the ICS A and sample concentrations of the interferents (Al, Ca, Fe, and Mg) are comparable or higher than those found in the ICS A, qualify detected results < 10x the absolute value of the negative result for the affected element as estimated biased low (J-) and nondetects (UJ).

<u>**Note**</u>: If the levels of interferents in the samples are comparable to or higher than those found in the samples, it may be appropriate to calculate the estimated interference for the analytes of interest using the following equation. Information on the impact of the calculated interference on the results for the analytes of interest may be included in the validation memorandum.

$$\text{Calculated Estimated Intereference} = \frac{\text{Interferent in sample}}{\text{Interferent in ICS A}} \times \text{element concentration in ICSA}$$

All criteria were met: ____
Criteria were not met, and/or see below: ____

VII. MATRIX SPIKE (MS) RESULTS

This data is generated to determine the effect of each sample matrix on sample preparation procedures and the measurement methodology.

1. Frequency Criteria

A. Was the MS analysis performed on a site-specific sample? If no, results are not evaluated due to potential differences in sample matrix. — Yes or No

B. Was an MS prepared at the required frequency (1 / batch / 20 samples / matrix)? — Yes or No

C. Was a Post digestion spike (PDS) performed for any analytes that fail MS %R criteria? (recommended for a new or unusual matrix and NA for CVAA) — Yes or No

D. Was a matrix spike/matrix spike duplicate (MS/MSD) analyzed in place of or in addition to a laboratory duplicate analysis? If yes, refer to Section VIII for calculations of RPDs from MS/MSD results. — Yes or No

2. Recovery Criteria

List the %Rs for analytes, which did not meet the criteria.

Sample # ____________ Matrix: ____________ Units: ____________

Analyte	MS/MSD Spiked Sample Result (SSR)	Sample Result (SR)	Spike Added (S)	MS/MSD %R	Action

Criteria: %R = 75-125% or project-specific QC limits (LL – lower limit, UL – upper limit).

Actions: MS actions apply to all samples of the same matrix. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

1. If the sample result (SR) > 4x the spike concentration (S), no action is taken.
2. If any analyte does not meet the %R criteria and a Post Digestion Spike analysis was performed, use professional judgement to assess the results. Refer to the National Functional Guidelines for recommended actions.
3. If either the MS or MSD does not meet %R criteria, qualify all associated samples.

Qualify results	MS %R in the Sample		
	%R < 30%	%R = 30%- 74% or 30% to LL	%R > 125% or > UL
Detected results	J-	J-	J+
Nondetects	R	UJ	A

All criteria were met: ____
Criteria were not met, and/or see below: ____

VIII. LABORATORY DUPLICATE RESULTS

Laboratories run duplicate samples to verify laboratory consistency and precision. They are a measure of laboratory performance. It is expected that soil/sediment duplicate results will have a greater variance than water matrices due to difficulties associated with preparing identical duplicate samples.

1. Frequency Criteria

A. Was the duplicate analysis or MSD analysis performed on a site -specific sample? If no, results are not evaluated due to potential differences in sample matrix. Yes or No

B. Was a duplicate or MSD analysis prepared at the required frequency (1 /batch /20 samples /matrix)? Yes or No

2. Precision Criteria: List the RPDs for analytes which did not meet the criteria.

Sample # ____________ Matrix: ____________ Units: ____________

For the soil matrix, calculate the sample quantitation limit (RL based on PQL) in mg/kg using the amount, volume, and % solids data for the sample. In some cases the lab may run an MS/MSD in place of a duplicate. Calculate RPDs from MS/MSD results.

Element	QL (ug/L)	QL (mg/Kg)	Sample or MS Result	Duplicate or MSD Result	RPD (%)	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Criteria:
RPD ± 20% for aqueous, RPD ± 35% for soil samples, if sample and duplicate results ≥ 5x QL.
QC limits of ± QL for aqueous, ± 2x QL for soil samples, if sample or duplicate result < 5x QL.

Actions: Indicate which criteria were used to evaluate precision by circling either the RPD or QL. If both samples are nondetected, the RPD is not calculated (NC), precision is considered acceptable. No action is needed.
If RPD is exceeded and sample or duplicate results are ≥ 5x QL, estimate detected results and nondetects (J/UJ).
If RPD is exceeded and sample or duplicate result is < 5x QL (including nondetects) and absolute difference between sample and duplicate is > QL for waters or > 2x QL for soils, estimate detected results and nondetects (J/UJ).

All criteria were met: ____
Criteria were not met,
and/or see below: ____

IX. FIELD DUPLICATE RESULTS

Field duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and lab precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

If appropriate, list the analyte concentration not meeting RPD criteria. For soil matrix, calculate the sample quantitation limit in mg/kg using the amount, volume, and %solids data for the sample.

Sample#____________Duplicate#_____________Matrix:________Units:_______

Element	QL (ug/L)	QL (mg/Kg)	Sample Result	Duplicate Result	RPD (%)	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Field duplicate actions should be applied to all other samples of the same matrix type. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

Criteria:

RPD $\pm$ 30% for aqueous, $\pm$ 50% for soils, if sample and duplicate results $\geq$10x QL.
Absolute difference of $\pm$ 4x QL for aqueous, $\pm$ 8x QL for soils if sample and duplicate <10x QL.
RPD and absolute difference must be exceeded if one result $\geq$ 10x QL and one <10x QL.

Actions:

Indicate which criteria were used to evaluate precision by circling either the RPD or QL. If both samples are nondetected, the RPD is not calculated (NC), no action is needed.

- If RPD is exceeded and sample results are $\geq$ 10x QL, estimate detected results and nondetects (J/UJ).
- If RPD is exceeded and sample or duplicate result is < 10x QL, estimate detected results and nondetects (J/UJ) for elements whose absolute difference is > 4x QL for waters and > 8x QL for soils.
- If RPD is NC because one result is $\geq$ 10x QL and one nondetect, estimate detected results and nondetects (J/UJ).
- If RPD is NC because one result is < 10x QL and one nondetect, use professional judgement.

All criteria were met: ____
Criteria were not met, and/or see below: ____

X. LABORATORY CONTROL SAMPLE (LCS) RESULTS

The assessment of the LCS(s) is to monitor the overall performance of each step during the analysis, including the sample preparation and determine matrix specific precision and accuracy.

Recovery Criteria: List any LCS results not within project-specific criteria, laboratory established control limits or National Functional Guideline recovery criteria.

Indicate which criteria were used: ______________________________

AQUEOUS LCS

Date	Analyte	%R	Action	Samples Affected

Note: NFGs have no control limits for Ag and Sb; however, include Ag and Sb in professional judgment. Apply actions to all samples in the same preparation batch.

Actions:

Aqueous LCS:	%R < 50%	%R = 50 – lower limit or 80%	%R > upper limit or 120%	%R >150%
Positive Sample Results	J-	J-	J+	R
Nondetects	R	UJ	A	R

SOLID LCS

Date	Analyte	LCS Conc.	QC Windows	Action	Samples Affected

Criteria: LCS results must be within the QC windows provided by the vendor. In absence of vendor limits use aqueous LCS control limits.

Note: Apply actions to all samples in the same preparation batch.

Actions:

Solid LCS	Less than Lower Acceptance Limit	Greater than Upper Acceptance Limit
Positive Sample Results	J-	J+
Nondetects	UJ	Accept

2. Frequency Criteria

Was an aqueous LCS analyzed with each batch of aqueous samples digested or for every group of aqueous samples in an SDG, whichever is more frequent? Yes or No

Was an solid LCS analyzed with each batch of solid samples digested or for every group of soil/sediment samples in an SDG ,whichever is more frequent? Yes or No

If no, data quality may be jeopardized. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions and list affected samples.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XI. SERIAL DILUTION ANALYSIS

The assessment of the serial dilution analysis is to determine the effect of the sample matrix on the accuracy of the results.

Were serial dilutions (1:5 dilutions) performed for each matrix and the results of the diluted sample analysis agreed within 10% difference (%D) of the original undiluted analysis for analyte concentrations >50x the IDL or MDL before dilution? Yes or No

Serial dilutions were not performed for the following target analytes: (optional for Hg) Yes or No

Was the serial dilution anlaysis performed on a site-specific sample? If no, results are not evaluated due to potential differences in sample matrix. Yes or No

List the % Ds for analytes which did not meet the %D criterion (10%).

Sample #:____________________ Matrix:_______________ Units:_____________

Element	IDL/MDL	50x IDL/MDL	Sample Results	Corrected Serial Dilution Results	%D	Action
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						
Tin						

Attach a separate sheet for additional metals

Actions: Actions apply to all samples of the same matrix. This qualification will also be applied to the results of all samples within a given area of the site, if deemed appropriate.

Estimate detected results and nondetects (J/UJ) for elements with %Ds > 10.

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XII. SAMPLE QUANTITATION ASSESSMENT

The objective is to ensure that the reported sample quantitation results are accurate. Evaluate any technical problems not previously addressed, examine the raw data for any anomalies, verify that there were no transcription or reduction errors on one or more samples and that results fall within the linear range for ICP and within the calibration range for CVAA.

1. Instrument Detection Limits/Method Detection Limits (IDL/MDL)/Quantitation Limits (QLs):

   A. Were results reported down to IDL/MDL or QL? (Circle one) IDL/MDL or QL

   B. Were IDL/MDL or QL results for all elements reported at levels that meet project objectives? Yes or No
   If not, indicate affected elements:

   C. If appropriate, estimate (J) results between the IDL/MDL and QL (refer to project-specific QAPP). Attach a separate sheet listing the qualified samples and analytes.

2. Reporting requirement:

   A. Were sample weights (including dry weights), volumes, and dilutions taken into account when reporting results (positive and nondetects)? If no, the reported results may be inaccurate. Request that the laboratory resubmit the corrected data. Yes or No

   B. Did sample results fall within the linear dynamic range for ICP and within the calibration range for CVAA? Yes or No
   If no, were dilutions performed? Yes or No
   List the affected samples/elements/dilution factor :

   If no, and dilution was not performed, estimate results (J).
   List the affected samples/elements:

All criteria were met: ____
Criteria were not met,
and/or see below: ____

XII. SAMPLE QUANTITATION ASSESSMENT (continued)

Sample Quantitation (full validation only): The sample quantitation evaluation is to verify that there were no transcription or reduction errors and to verify laboratory sample quantitation on one or more samples. In the space below, please show a minimum of one sample calculation.

ICP by 6010B

Mercury by 7470A/7471A

For soil samples, the following equation may be necessary to convert raw data values reported in µg/L to actual sample concentrations (mg/kg):

$$\text{Conc. in } \mu g/L \times \frac{\text{Volume diluted to (ml)}}{\text{Weight digested (g)}} \times \frac{1L}{1000ml} \times \frac{1000\,g}{1kg} \times \frac{1mg}{1000\,\mu g} = \text{concentration in wet weight (mg/kg)}$$

In addition, the concentrations are converted to dry weight using the % solids calculation:

$$\frac{\text{Wet weight conc}}{\text{\% Solids}} \times 100 = \text{Concentration in dry weight (mg/kg)}$$

ENSR INTERNATIONAL

Laboratory/Location:		ENSR Data Package #:
Laboratory SDG/Job No:		Client/Site Name:
No. of Samples-Matrix:		Project Number:
Acceptance Criteria: QAPP/Method		Validation Actions:
Validator:	Date Checked:	Full / Limited Validation (circle one)

DATA PACKAGE COMPLETENESS CHECKLIST

ITEM	YES	NO	N/A	COMMENTS
Sample results included?				
Detection levels included?				
Field I.D. included?				
Laboratory I.D. included?				
Sample matrix included?				
Sample receipt temperature 2-6ºC?				
Sample preservation acceptable?				
Signed COCs included?				
Date of sample collection included?				
Date of sample prep. included?				
Date of analysis included?				
Method reference included?				
QC Documentation included?				
Case Narrative included				
Equipment/Field Blank IDs				
Field Duplicate IDs				

Definitions: IDL – Instrument Detection Limit; MDL – Method Detection Limit; RL – Reporting Limit; SQL = Sample Quantitation Limit; %RSD – Percent Relative Standard Deviation; %D – Percent Difference; %R – Percent Recovery; RPD – Relative Percent Difference; r – correlation coefficient; LCS – Laboratory Control Sample; NFG – National Functional Guidelines

Comments	Review Element	Criteria*	Action
	Preserv.:	See method	Use prof. judgment
	HT:	See method	J-/UJ if exceeded
	Calib. curve Cyanide Other	$r \geq 0.995$ 100 ±15% 100 ±10%	Use prof. judgement J+ if exceeded J-/UJ if below
	Blank	< RL	Refer to NFG
	MS/MSD	%R= 75-125% RPD ±20%	J+ if %R > 125 J-/UJ if %R < 75 J if RPD exceeded
	Lab Dup	Aq. RPD ±20% So. RPD ±35%	J if RPD exceeded
	Field Dup (ENSR)	Aq. RPD ±30% So. RPD ±50%	See ENSR DV actions
	LCS/LCSD	%R= 75-125% RPD ±30%	J+ if %R > 125 J-/UJ if %R < 75 J if RPD exceeded
	* If no criteria specified by the method, lab, or QAPP, use these QC limits as guidance.		

ENSR INTERNATIONAL

QA/QC CHECKLIST FOR GENERAL CHEMISTRY ANALYSIS

ITEM	YES	NO	N/A	COMMENTS
PARAMETER:		METHOD:		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
PARAMETER:		METHOD:		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
PARAMETER:		METHOD:		
Calibration Info Included in Lab Package?				
Criteria met? (%RSD, r, %Rs)				
Method Blank Data Included in Lab Package?				
Criteria met? (< RL)				
Field/Equipment Blank Included in Lab Package?				
Criteria met? (< RL)				
Matrix Spike (MS) Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				
MS Duplicate or Lab Dup Data Included in Lab Package?				
%R or RPD criteria met? (Method or Lab or QAPP)				
Field Duplicate Included in Lab Package?				
RPD criteria met? (QAPP OR ENSR)				
QC Check Samples/LCS Data Included in Lab Package?				
%R criteria met? (Method or Lab or QAPP)				

Use this space for notes/comments and/or spot check calculation (if required)

ATTACHMENT E-2

RADIOCHEMISTRY DATA VALIDATION PROTOCOLS

ENSR

DATA REVIEW WORKSHEETS

Type of Review Full:_____ Limited: ____

ENSR Data Pkg ID ______________
Site Name: ______________
Project Number: ______________

REVIEW OF RADIOLOGICAL DATA PACKAGE

The following guidelines for evaluating radiological data were created to delineate required review actions. This document will assist the reviewer in using professional judgement to make more informed decisions and in better serving the needs of the data users. The radiological data will be reviewed based on method compliance and quality control (QC) results to provide a level of assurance that an nuclide is present or absent. The level of uncertainty (bias) associated with the reported result will be indicated, if applicable. The evaluation of the radiological data will be evaluated based on the Department of Energy *Evaluation of Radiochemical Data Usability (1997)*. However, the QC samples will not be evaluated based on a statistical level of confidence as discussed in the *Evaluation of Radiochemical Data Usability (1997)*, but rather to the laboratory QC acceptance criteria, unless otherwise indicated.

The hardcopied (laboratory name) ______________ data package received has been reviewed and the quality control (QC) and performance data summarized. The review of radiological data included:

Lab Project/SDG No.: ______________________________
Sample Matrix: ______________________________
No. of Samples: ______________________________
Field Blank ID: ______________________________
Equipment Blank ID.: ______________________________
Field Duplicate IDs.: ______________________________

List analyses reviewed and analytical method: ______________ ______________
______________ ______________
______________ ______________

The general criteria used to determine performance were based on an examination of (check all that apply):

____ Data Completeness
____ Holding Times/Sample Preservation
____ Method Blank
____ Chemical Yield (Tracers and Carriers)
____ Laboratory Control Sample (LCS)
____ Calibration
____ Matrix Spike/Matrix Spike Duplicate (MS/MSD)
____ Laboratory Duplicates
____ Field Duplicates
____ Sample Identification and Quantitation
____ Reporting Limits

Overall Comments: ____
____
____

Definitions and Qualifiers:

U - Nuclide considered not detected above the reported Minimum Detectable Concentration (MDC) or 2 sigma counting uncertainty
J - Nuclide identified; the associated numerical value is estimated
UJ - Nuclide is not detected above the reported MDC or 2 sigma counting uncertainty; the reporting limit may be inaccurate or imprecise
R - Result is rejected and is not usable for project objectives

In general, only one qualifier is permitted with each result. Qualifiers relating to identification (U or R) take precedence over qualifiers relating to quantitation (J or UJ). Whenever an "R" is used for nondetects, "UJ" is not used. Within each category of qualifiers, use the qualifier that indicates a more serious problem.

Reviewer: ______________________________ Date: ______________

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

I. DATA COMPLETENESS

A. Data Package:

_______ The tests requested on the COC or in subsequent communications were performed and reported

_______ The correct nuclide list was reported

_______ The COCs (external and internal) are present and properly completed

_______ Sample receiving documentation is complete

Missing Information	Date Lab Contacted	Date Received

B. Other Discrepancies

Codes

SR – Sample Results
BR – Blank Result
MDC – Minimum Detectable Concentration
TPU – Total Propagated Uncertainty
RL- Reporting Limit

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

II. HOLDING TIMES

The objective of this parameter is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of sample analysis (activity detection). Samples must be analyzed prior to significant decay of short-lived target radionuclides. Complete the table for all samples and circle the analysis date for samples not within criteria.

SAMPLE ID	DATE SAMPLED	GROSS ALPHA DATE ANALYSIS	GROSS BETA DATE ANALYSIS	ISOTOPIC URANIUM DATE ANALYSIS	ISOTOPIC THORIUM DATE ANALYSIS	pH	ACTION

Cooler Temperature: ____________________

Criteria:

- Analysis Holding Times: no technical holding times due to long half lives, but 6 months from sample collection (for contractual reasons)
- Sample Preservation: Concentrated HCL or HNO_3 to pH ≤ 2

Actions:

If samples not preserved properly in the field or laboratory and/or stored in improper container, then:
- SR < sample MDC qualify as estimated "UJ".
- SR $\geq$ sample MDC use professional judgment to qualify as estimated "J"

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

II. HOLDING TIMES (continued)

The objective of this parameter is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of sample analysis (activity detection). Samples must be analyzed prior to significant decay of short-lived target radionuclides. Complete the table for all samples and circle the analysis date for samples not within criteria.

SAMPLE ID	DATE SAMPLED	Ra-226 DATE ANALYSIS	Ra-228 DATE ANALYSIS	Tc-99 DATE ANALYSIS	Tritium DATE ANALYSIS	pH	ACTION

Cooler Temperature: ______________________

Criteria:

- Analysis Holding Times: no technical holding times due to long half lives, but 6 months from sample collection (for contractual reasons)
- Sample Preservation: Concentrated HCL or HNO_3 to pH ≤ 2 for gross alpha or beta, Ra-226, Ra-228, isotopic uranium, isotopic thorium, and Tc-99

Actions:

If samples not preserved properly in the field or laboratory and/or stored in improper container, then:

- SR < sample MDC qualify as estimated "UJ".
- SR $\geq$ sample MDC use professional judgment to qualify as estimated "J"

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

III. BLANK ANALYSIS RESULTS

The assessment of the blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples, including equipment, field, and laboratory blanks.

If problems with any blanks exist, all data associated with the case must be carefully evaluated to determine whether or not there is an inherent variability in the data for the case, or if the problem is an isolated occurrence not affecting other data.

1. Frequency Requirements

Was a method blank analyzed at the frequency stated in the method or by the project? Yes or No
Was the method blank the same matrix as the sample in the batch? Yes or No

If no, the data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below, and list the samples affected.

____

____

2. Blank Actions

The method blank activities must be less than their MDC and 2 sigma counting uncertainty.

Blanks must be evaluated in the following order:
- Method blanks must first be used to qualify equipment/field blanks and samples.
- Contamination remaining in the equipment/field blanks will be used to qualify the associated samples.

Actions:
- if blank results < MDC or < 2 sigma counting uncertainty – no action
- if blank results > MDC , but SR < sample MDC – no action
- if blank results > MDC and SR > sample MDC or 2 sigma counting uncertainty, then
  - determine normalized absolute difference between blank and SR using

$$\frac{\text{Absolute Difference (SR} - \text{BR)}}{\text{Square Root }(TPU^2_{SR} + TPU^2_{BR})}$$

If normalized absolute difference > 2.58, no qualification
If normalized absolute difference between 1.96 and 2.58, qualify SR $\geq$ MDC as estimated "J"
If normalized absolute difference between 0 and 1.96, use professional judgment to "R"

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DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

III. BLANK ANALYSIS RESULTS (continued)

List the contamination > MDC or RL in Sections A & B below.

A. Method blanks

Matrix: __________ Unit ______________

Date Analyzed	MB ID	Nuclide	Concentration	RL	Affected Samples

B. Field/Equipment blanks

Date Collected	Field ID	Nuclide	Concentration	RL	Affected Samples

C. Normalized Absolute Difference

Sample ID	Nuclide	SR + TPU	BR + TPU	Normalized Absolute Difference	Action

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

IV. CHEMICAL YIELD (TRACERS AND CARRIERS)

Tracers and carriers used in radiochemical separation methods are used to evaluate chemical separation.

1. Frequency Requirements

Were carrier or tracer percent recoveries reported for each sample? Yes or No

If no, the data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

2. Carrier or Tracer Recovery

List samples that have carrier or tracer percent recoveries (%Rs) outside criteria.

Sample ID	Nuclide	%R	Action

Criteria: %R = 25-125% for isotopic uranium

Actions: Do not qualify data on yield results alone. If carrier or tracer %Rs are low, there may be increased uncertainty in the SR (MDC > RL). If the yield is low, but the LCS %Rs are acceptable, then accept data without qualification.

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

V. LABORATORY CONTROL SAMPLE (LCS)

The assessment of the LCS(s) is to monitor the accuracy of preparation and analysis.

1. Recovery Criteria

List LCS percent recoveries (%Rs) or normalized differences not within the criteria and the samples affected.

Date	Nuclide	%R/Normalized Difference	Action	Sample Affected

Criteria: ____ %R = 75-125% or _____ list other %R or ____ Normalized Difference

Actions:

If %R criteria used then follow the actions stated below:

LCS	%R < 10%	%R = 10 – LL%	%R > UL%
Detected Sample Results	R	J	J
Nondetected Results	R	UJ	Accept

LL – lower limit UL – upper limit

If normalized difference criteria used then follow the actions stated below:

LCS	Negative bias less than -2.58	Negative bias between -1.96 and -2.58	Between -1.96 and 1.96	Positive bias between 1.96 and 2.58	Positive bias greater than 2.58
Sample Results ≥ MDC	R*	J	Accept	J	R*
Sample Results < MDC	R*	UJ	Accept	Accept	Accept

* Consider the effects of other QC samples prior to qualifying

2. Frequency Criteria

Was an LCS analyzed with each batch? Yes or No
Was the LCS analyzed on the same detection system as the samples? Yes or No

If no, data quality may be jeopardized. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions and list affected samples.

ENSR

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

VI. MATRIX SPIKE/MATRIX SPIKE DUPLICATE (MS/MSD)

1. Recovery Criteria

Sample # ____________ Matrix: ____________ Units: ____________

This data is generated to determine long-term precision and accuracy of the analytical method for various matrices.

List MS/MSD percent recoveries (%Rs) or normalized differences not within the criteria and the samples affected.

Nuclide	Spiked Sample Result (SSR)	Sample Result (SR)	Spike Added (S)	%R	%RPD	Normalized Difference	Action

Criteria: ____ %R = 75-125% or _____ list other %R or ____ Normalized Difference

Actions: MS/MSD actions apply to the field sample used for the MS/MSD analyses. This qualification may also be applied to the results of all samples within a given area of the site or preparation batch, if deemed appropriate.

If %R criteria used then follow the actions stated below:

Qualify Results	MS and/or MSD %R			-20%< %RPD >20%
	%R < 10%	%R = 10 - LL%	%R > UL%	
Detected Results	J	J	J	J
Nondetected Results	R	UJ	Accept	UJ

LL – lower limit UL – upper limit

If normalized difference criteria used then follow the actions stated below:

LCS	Negative bias less than -2.58	Negative bias between -1.96 and -2.58	Between -1.96 and 1.96	Positive bias between 1.96 and 2.58	Positive bias greater than 2.58
Sample Results $\geq$ MDC	R*	J	Accept	J	R*
Sample Results < MDC	R*	UJ	Accept	Accept	Accept

* Consider the effects of other QC samples prior to qualifying

2. Frequency Criteria

Was a matrix spike prepared at the frequency stated in the method or by the project? Yes or No
Were all nuclides or interest spiked into the MS/MSD? Yes or No or NA

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

VII. LABORATORY DUPLICATES*

Sample #____________ Matrix: ____________ Units: ____________

Laboratories run duplicate samples to verify laboratory consistency and precision. They are a measure of laboratory performance. It is expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with preparing identical duplicate samples.

List nuclide not meeting the RPD or Normalized Absolute Difference (circle criteria used).

Nuclide	MDC	RL	Sample Results	Duplicate Results	RPD (%)	Normalized Absolute Difference	Action

Laboratory duplicate actions should be applied to the field sample used as the laboratory duplicate. This qualification may also be applied to the results of all samples within a given area of the site and/or preparation batch, if deemed appropriate.

Criteria:

- RPD ± 20% for aqueous, RPD ± 35% for soil samples, if sample and duplicate results ≥ 5x RL or MDC.
- QC limits ± RL or MDC for aqueous, ± 2x RL or MDC for soil samples, if sample/duplicate results < 5x RL or MDC.
- Normalized absolute difference less than or equal to 1.96

Actions: Indicate which criteria were used to evaluate precision by circling RPD, RL, or MDC. If both samples are nondetected, precision is considered acceptable. No action is needed.

- If RPD is exceeded and sample results are ≥ 5x RL or MDC, estimate detected results and nondetects (J/UJ).
- RPD is exceeded and sample or duplicate result is < 5x RL or MDC, estimate detected results and nondetects (J/UJ) for nuclides whose absolute difference is > RL or MDC for waters or > 2x RL or MDC for soils.
- If normalized absolute difference is greater than 1.96, estimate results (J/UJ)

2. Frequency Criteria

Was a laboratory duplicate prepared and analyzed with each batch of up to 20 samples? Yes or No

*A separate worksheet page should be used for each laboratory duplicate

ENSR

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

VIII. FIELD DUPLICATES*

Sample #____________ Matrix: ____________ Units: ____________

Field duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and lab precision; therefore, the results may have more variability than lab duplicates which measure only lab performance. It is also expected that solid matrices will have a greater variance than water matrices due to difficulties associated with collecting identical field duplicate samples.

List nuclide not meeting the RPD or Normalized Absolute Difference (circle criteria used).

Nuclide	MDC	RL	Sample Results	Field Duplicate Results	RPD (%)	Normalized Absolute Difference	Action

Field duplicate actions should be applied to the field duplicate pair. This qualification may be applied to the results of all samples within a given area of the site and/or preparation batch, if deemed appropriate.

Criteria:

- RPD ± 30% for aqueous, ± 50% for soils, if sample and duplicate results ≥ 10x RL or MDC.
- Absolute difference ± 4x RL or MDC for aqueous, ± 8x RL or MDC for soils, if sample and duplicate < 10x RL or MDC.
- RPD and absolute difference must be exceeded if one result ≥ 10x RL and one < 10x RL.
- Normalized absolute difference less than or equal to 1.96

Actions: Indicate which criteria were used to evaluate precision by circling RPD, RL, or MDC. If both samples are nondetected, precision is considered acceptable. No action is needed.

- If RPD is exceeded and sample results are ≥ 10x RL or MDC, estimate detected results and nondetects (J/UJ).
- If RPD is exceeded and sample or duplicate result is < 10x RL or MDC, estimate detected results and nondetects (J/UJ) for elements whose absolute difference is > 4x RL or MDC for waters or > 8x RL or MDC for soils.
- If RPD is NC because one result ≥ 10x RL or MDC and one nondetect, estimate detected and nondetects (J/UJ).
- If RPD is NC because one result < 10x RL or MDC and one nondetect, use professional judgment. Laboratory duplicate actions should be applied to the field sample used as the laboratory duplicate.
- If normalized absolute difference is greater than 1.96, estimate results (J/UJ)

2. Frequency Criteria

Was a laboratory duplicate prepared and analyzed with each batch of up to 20 samples? Yes or No

*A separate worksheet page should be used for each laboratory duplicate

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

IX. CALIBRATION

1. Standard Traceability

   a. Were certificates included for calibration standards, LCS, and/or MS/MSD? Yes or No
   b. Did certificate serial numbers match referenced standards? Yes or No
   c. Were the standards within the expiration dates? Yes or No

   If no, list standards affected

Standard ID	Nuclide	Lab ID	Certificate ID	Expiration Date

2. Calibration Verification

   a. Are the efficiencies within the appropriate control criteria? Yes or No
   b. Are instrument backgrounds within the appropriate control criteria? Yes or No
   c. Are energies within the appropriate control criteria? Yes or No
   d. Peak resolution within appropriate control criteria? Yes or No

   If no, list standards affected

Standard ID	Nuclide	Lab ID	Certificate ID	Expiration Date

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

X. SPECTRAL INTERPRETATION

1. Gamma Analyses

a. Do isotopes of the same radionuclide show secular equilibrium? Yes or No
b. Soil samples: are peaks at 511 keV (annihilation peak) and 1460 keV (K-40) present? Yes or No
c. Are all detected peaks correctly identified? Yes or No
d. Do peaks overlap? Yes or No

If yes, list affected samples and nuclides

Sample ID	Nuclide	Peak Energy	Estimated % Overlap	Action

2. Alpha Spectra

a. Are target peaks within the energy range of interest (ROI)? Yes or No
b. Does peak overlap exist through tailing from other nuclides? Yes or No
If yes, list samples and nuclides affected by tailing below:

Sample ID	Nuclide	Issue

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DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

XI. SAMPLE IDENTIFICATION AND QUANTITATION

1. Are sample results > sample MDCs? Yes or No
   If no, qualify SRs as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR MDC	Action

2. Are sample results > 2 sigma counting uncertainty? Yes or No
   If no, qualify SRs as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR MDC	Action

Use Professional judgment in cases where:
- SR < MDC, but > 2 sigma counting uncertainty may have been counted long enough to be considered detected.
- SR > MDC, but < 2 sigma counting uncertainty may NOT have been counted long enough to be considered detected.

3. Are sample results > 2 TPU? Yes or No
   If no, qualify sample results (SRs) as "U". List samples and nuclides below

Sample ID	Nuclide	SR	SR TPU	Action

Use Professional judgment in cases where:
- SR < MDC, but > 2 sigma counting uncertainty may have been counted long enough to be considered detected.
- SR > MDC, but < 2 sigma counting uncertainty may NOT have been counted long enough to be considered detected.

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

4. Negative Sample Results

Negative results with absolute values greater than their 2 sigma counting uncertainty indicate that the instrument background may have shifted. Use professional judgment to qualify data.

Do negative sample results have absolute values > 2 sigma counting uncertainty? Yes or No
If yes, list samples and nuclides below:

Sample ID	Nuclide	SR	SR 2 sigma uncertainty	Action

5. Gross values vs total of individual nuclides

Are gross alpha results > total of individual uranium results Yes or No
If no, list samples with gross alpha < total of individual uranium isotopes

Sample ID	Gross alpha SR	Total of individual uranium isotopes	Action

Action

- if gross alpha < total of individual isotopic uranium, then estimate (J) detected individual U results if applicable in affected sample.

DATA REVIEW WORKSHEETS

All criteria were met: ______
Criteria were not met,
and/or see below: ______

XII. REPORTING LIMITS

1. Minimum Detectable Concentration (MDC)

   A. Were sample MDCs < RLs? Yes or No

   B. Determine why the MDC> RL (ex. small sample size, inadequate count time, or matrix problems). If sample MDC > RL and SR < sample MDC or $\pm$ 2 sigma counting uncertainty, and there is no justification for not reanalyzing at a longer count time or greater sample aliquot, then data are noncompliant with RL – note in report. The data may be affected. Use professional judgment to determine the severity of the effect and qualify the data accordingly. Discuss any actions below and list the samples affected.

____
____
____
____
____
____
____
____
____

2. Aliquot Size

List samples and nuclides that required adjusted aliquot size.

Sample ID	Nuclide	Aliquot Size

A representative sample aliquot must be chosen to ensure the dissolved solid content of the sample falls within the mass range of the appropriate curve. Sample results for which aliquot weight is outside the attenuation curve should be qualified as estimated (J) if not reanalyzed with a smaller aliquot.